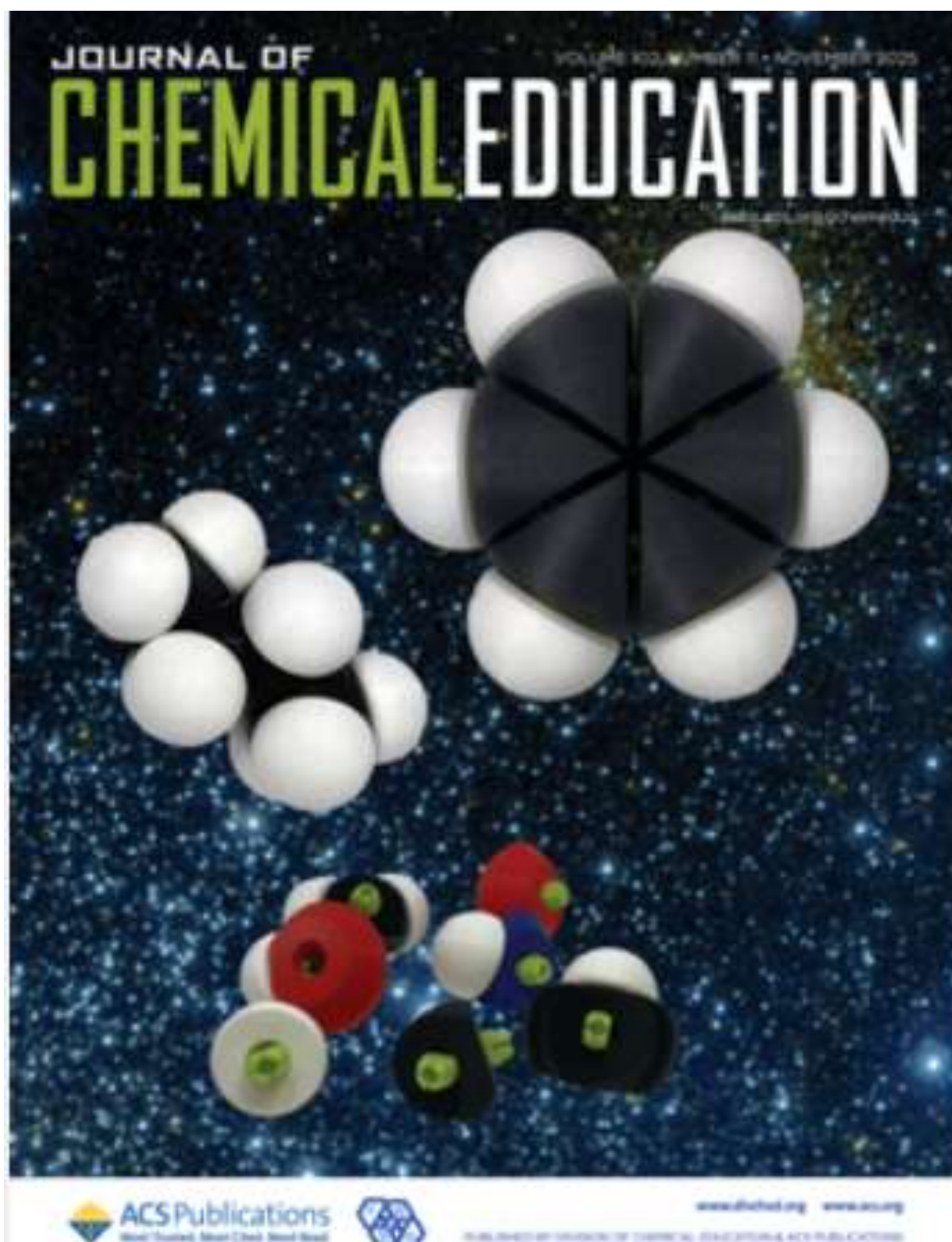


Journal of Chemical Education

- publications by Gavin D Peckham



Chronological list of articles published in J Chem Educ by Gavin D Peckham

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1984, 61 (10), 868.	Illustrating the Heisenberg uncertainty principle.
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1987, 64 (12), 999	Two fundamental constants.
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1998, 75 (1), 49	The Electromotive Series and Other Non-Absolute Scales.
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2009, 86 (3), 330	Effects of Hydrolysis on Determining K_{sp} of Potassium Bitartrate.
2011, 88 (5), 592	Teaching Two-Component Phase Diagrams.
2011, 88 (6), 782	The Variation of Electrochemical Cell Potentials with Temperature.
2012, 89 (4), 557	The Octant Rule: Check UPFRont.
2012, 89 (7), 955	Teaching Intermolecular Forces to First-Year Undergraduate Students.

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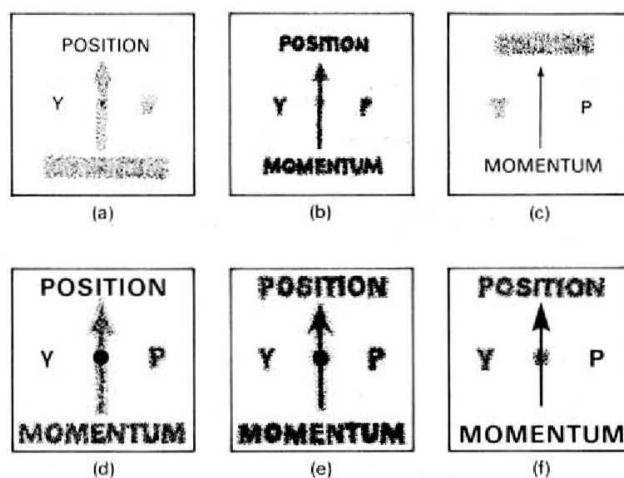
Illustrating the Heisenberg Uncertainty Principle

Cosser has shown how, at an elementary level, Heisenberg's Uncertainty Principle (HUP) may be illustrated using an overhead projector and a pair of transparencies labelled "POSITION" and "MOMENTUM," mounted in a frame, one above the other.¹ Students tend to imagine that the HUP suddenly becomes magically apparent only at the atomic level and fail to appreciate that the HUP is generally applicable, but that its significance decreases as the dimensions of the system increase.

The overhead projector analogy may be carried to illustrate this point by the use of two pairs of transparencies. Both pairs carry similar inscriptions. However, the inscription on one pair is formed with large, thick print, while the second pair carries small, fine print. The relative size of the print on each pair of transparencies is not critical, but a large difference between the thickness of the print is desirable.

The result of the HUP on a system of small dimensions may be illustrated using the finely printed pair of transparencies. By focussing more clearly on one transparency, the other becomes more blurred. Eventually when one transparency is in sharp focus, the other is undiscernable. The intermediate and extreme cases are shown in parts (a), (b) and (c) of the figure. The results of the HUP on a system of larger dimensions may be illustrated using the heavily printed transparencies. The same tendency for preferential focussing will be found, but at the extreme case when one transparency is in sharp focus, the other will be only somewhat less legible. These possibilities are shown in parts (d), (e) and (f) of the figure.

For systems of everyday dimensions, of course, the HUP diminishes into insignificance.



¹ Cosser, R. C., J. CHEM. EDUC., 59, 300 (1982)

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Determination of Molecular Dimensions Using Monolayers: Another Approach

The ability of oil to spread across a water surface has been known for hundreds of years. As long ago as 1773, Benjamin Franklin observed, on a pond near London, that one teaspoon of oil would spread to form a film with an extent of about 22,000 ft² (1).

The estimation of Avogadro's number and of molecular dimensions by the "Oil Drop Experiment" was first presented by King and Neilsen (2) who based their experiment on the techniques of earlier workers (3-5). The experiment has become popular in laboratory manuals for general chemistry courses (6-8) and various authors have suggested improvements, refinements, and variations on the theme (9-13).

Beginning students in chemistry sometimes find it difficult to conceptualize the principles involved and are often skeptical about the accuracy of the results. We have greatly reduced this problem by introducing an analogous experiment as a preliminary to the oil drop experiment itself. The experimental analogy is outlined below.

- 1) Determine the "volume" of about 8 mL of 2-mm ball bearings using a graduated cylinder. (These ball bearings are available in bulk from most bicycle manufacturers.)
- 2) Empty the ball bearings onto a large watchglass and pat them down to form a monolayer.
- 3) Make several measurements to determine the average diameter and hence the area of the monolayer.
- 4) Use the volume and area to calculate the height of the monolayer. This height corresponds to the diameter of the individual ball bearings, thus the result may be verified by direct measurement of the ball bearings' diameters.

This experiment enables a student to clearly visualize the oil drop experiment and enables him or her to confirm the accuracy of the results. The usual discussion of experimental errors and assumptions, particularly those concerning molecular shapes and packing can be applied to this analogy.

The experiment may be prepared and performed easily and quickly. It utilizes cheap, reusable equipment. If time or equipment is a limiting factor then the experimental analogy may be carried out by the students themselves, followed by a demonstration of the actual oil drop experiment by the instructor. Conversely, if the students are to perform the oil drop experiment themselves, then a demonstration of the ball bearing analogy by the instructor provides a useful introduction.

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[A⁻] in Weak Acid Solution

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The cubic equations that arise when accurately calculating the concentrations of the various species of a monobasic acid or base in solution have recently attracted some attention in THIS JOURNAL. Ladd² gives the two cubic equations that must be satisfied by [H⁺] and [A⁻]

$$[H^+]^3 + K_a[H^+]^2 - (K_a c + K_w)[H^+] - K_a K_w = 0 \quad (1)$$

$$[A^-]^3 + (K_a - c - K_w/K_a)[A^-]^2 - 2K_a c[A^-] + K_a c^2 = 0 \quad (2)$$

where c is the analytical concentration of the weak acid and K_a is its dissociation constant. It is easy to show that eq 2 has two positive roots so some ambiguity may arise, particularly if an iterative technique is used to solve for only one root. This ambiguity can be eliminated by noting that [A⁻] is *uniquely* determined by [H⁺], viz.

$$[A^-] = cK_a/([H^+] + K_a) \quad (3)$$

Equation 1 has only one positive root so [H⁺] can be determined unambiguously. Equation 3 then gives [A⁻] uniquely.

Ladd's criticism of Levy and Byers' quadratic equation³ is invalid. The concentration of A⁻ calculated from their equation is negligibly different from that obtained by solving the complete cubic equation. The misconception arises because the roots of the cubic equation given by Ladd are slightly (but significantly) wrong at a concentration of 10⁻⁴ mol dm⁻³ and very wrong at a concentration of 10⁻⁶ mol dm⁻³.

¹ Author to whom correspondence should be addressed.

² Ladd, M. F. C. *J. Chem. Educ.* **1980**, *57*, 669.

³ Levy, M.; Byers, L. D. *J. Chem. Educ.* **1979**, *56*, 526.

Two Fundamental Constants

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It is rare for a beginning student in chemistry to measure well-known fundamental constants. The experiment described here can give accurate values for both the absolute zero of temperature and the gas constant using very simple apparatus. Several descriptions of experiments that determine these constants have appeared in *this Journal* (1–5). In general they employ small volumes at just a few different temperatures. The very small change in volume is difficult to measure accurately, and no sensible statistical analysis of errors is possible with so few readings.

As has been noted by Davenport (6), greater precision can be obtained if the change in volume is measured rather than the total volume. This approach is followed in the experiment described here, which uses a gas syringe to measure the change in volume of gas contained in a large Erlenmeyer flask.

Theory

Charles showed that at constant pressure the volume of any gas is directly proportional to the temperature. Different amounts of gas gave lines with different slopes but all the lines showed a particular characteristic, namely that when extrapolated to zero volume they all crossed the temperature axis at the same point; that is, for any gas

$$V = k(t + c) \quad (1)$$

where t is the temperature in degrees Celsius, c is a constant that is the same for all gases, and k is a constant that depends on both the amount of gas and the pressure. If the temperature scale is adjusted so that the temperature intercept is taken as the origin, then Charles's law takes the simple form

$$V = kT$$

where T is the temperature on the absolute scale.

The equation of state for an ideal gas can be written as

$$V = nRT/P \quad (2)$$

If the variation in volume of a gas with temperature is measured at known, constant pressure and number of moles, then it is possible to determine the gas constant from the slope of a plot of volume versus temperature while the absolute zero of temperature in degrees Celsius is obtained from the intercept on the temperature axis.

Experimental

A 100-cm³ gas syringe with a rubber bung on the outlet is set to zero and fitted to a clean, dry 500-cm³ flask. The flask as well as the barrel of the gas syringe are placed vertically in a water bath with an immersion heater. With the heater constantly operating, the volume is measured as a function of temperature over a temperature range of about 50 °C.

When the heating is complete the flask is removed from the bath, cooled to room temperature, and dried. Then the gas syringe is replaced by a stopcock. To determine the mass of gas in the flask, it is evacuated, weighed (on a three-place top-loading balance), and reweighed after the flask has been opened to the air. The volume of the flask is obtained from the mass of water required to fill it to the original level of the

bung. The atmospheric pressure and temperature are measured, as are the mass and the diameter of the gas syringe plunger.

Calculations

The most direct way to determine the absolute zero is to plot the change in total volume against temperature and extrapolate to zero total volume. The total volume is obtained by adding the gas syringe readings to the volume of the flask (obtained by dividing the mass of water in the flask by the tabulated density of water). However, because of the long extrapolation required, this is not the most accurate way to analyze the data.

Better results are obtained by using the following algebraic approach. The gas syringe volume measurements are plotted against the temperature and the equation of the best straight line is determined. The volume of the flask is then added to the constant term in the equation. Rearrangement of eq 1 into the standard form of a straight line ($V = a + bt$) shows that the absolute zero of temperature in degrees Celsius is given by the negative of the constant term divided by the slope, while eq 2 shows that the gas constant can be determined from the slope. The number of moles of gas is obtained from the mass of gas and its molar mass. If the gas used is air then its molar mass can be taken as 28.96 g mol⁻¹. The total pressure with which the gas is in equilibrium consists of that due to the atmosphere plus that due to the plunger.

Results

A typical set of results and the attendant calculations is given below.

Flask + stopcock (evacuated) = 199.311 g
Flask + stopcock + air = 199.866 g
∴ Mass of air = 0.555 g

Flask + air = 148.8 g
Flask + water = 649.4 g
∴ Mass of water = 501.1 g
Water temperature = 20.0 °C
Density of water = 0.9982 g cm⁻³
∴ Volume of water = 501.1/0.9982 cm³
= 502.0 cm³
= 5.020 × 10⁻⁴ m³

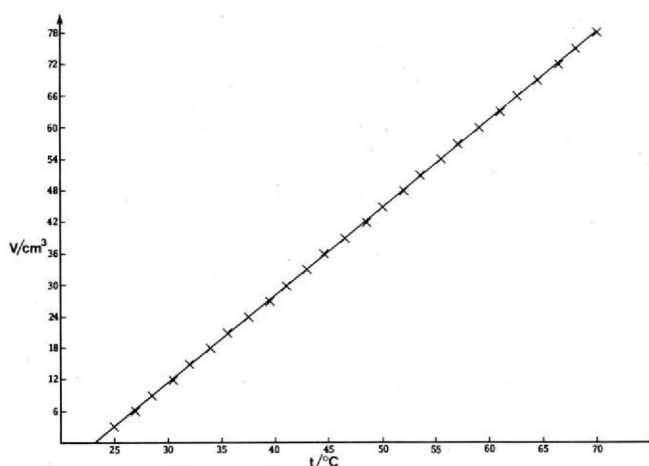
Mass of plunger = 95.310 g
Diameter of plunger = 3.20 cm
 $P(\text{plunger}) = \text{mass} \times \text{gravitational acceleration} / \text{plunger area}$
= 95.31 × 10⁻³ × 9.8 / 8.04 × 10⁻⁴ N m⁻²
= 1.2 kN m⁻²

Atmospheric pressure = 708 mm Hg (at our altitude of 700 m)
= 94.4 kN m⁻²
 $P = P(\text{atm}) + P(\text{plunger})$
= 94.4 kN m⁻² + 1.2 kN m⁻²
= 95.6 kN m⁻²

A typical plot of gas syringe volume as a function of temperature is given in the figure.

A least-squares fit of those data gives the equation

$$V = -38.72 \pm 0.18 + (1.671 \pm 0.004)t$$



Plot of gas syringe volume reading vs temperature.

When the volume of the flask is added, then the variation in total volume with temperature in degrees Celsius becomes

$$V = 463.3 \pm 0.4 + (1.671 \pm 0.004)t$$

It may be noted that the error in the constant term is now dominated by the error in determining the volume of the flask. Solving this equation to determine the temperature at which the volume goes to zero gives $t = -277 \pm 1^\circ\text{C}$ as the estimate of the absolute zero of temperature.

In determining the gas constant it is convenient to convert the measurements to SI.

$$\begin{aligned} \text{slope} &= nR/P \text{ (from eq 2)} \\ &= 1.671 \text{ cm}^3 \text{ K}^{-1} \\ &= 1.671 \times 10^{-6} \text{ m}^3 \text{ K}^{-1} \\ n &= 0.555/28.96 \text{ mol} \\ &= 0.0192 \text{ mol} \\ \therefore R &= 1.671 \times 10^{-6} \times 95.6 \times 10^3 / 0.0192 \\ &= 8.32 \pm 0.09 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

Discussion

Although the complete experiment can be done entirely in a single 3-hour session, it is possible to shorten it in several ways, for example by giving the students the volume of the flask and number of moles of gas contained in it as well as the pressure due to the plunger. This eliminates all the weighings, which could otherwise lead to a bottleneck in the absence of sufficient balances. If a somewhat lower accuracy is acceptable, then the volume of the flask can be determined by filling it with water to the bung level and then pouring the water into a graduated cylinder. This experiment not only enables the students to determine two fundamental constants but also emphasizes the need for careful attention to the conversion of units. In addition it demonstrates the need to consider the required accuracy in a measurement (e.g., the mass of gas must be determined to more decimal places than the mass of water). This helps to illustrate the distinction between decimal places and significant figures, a constant source of confusion for our students. Careful students who fit their data by least squares generally get standard deviations in the slope and intercept of less than 1%.

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Applications of Maxwell-Boltzmann Distribution Diagrams

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Maxwell-Boltzmann distribution diagrams can be used to aid the understanding of many topics of interest to the chemist. With a suitable introduction they can be readily implemented even at the high school level, but care must be taken to avoid several common errors and misconceptions.

Diagrammatic representations are usually grasped fairly easily, and they are intuitively appealing. Thus, the popularity of such diagrams in textbooks is very understandable. At an introductory level, however, we feel that the general form of these curves should not simply be presented as a fait accompli.

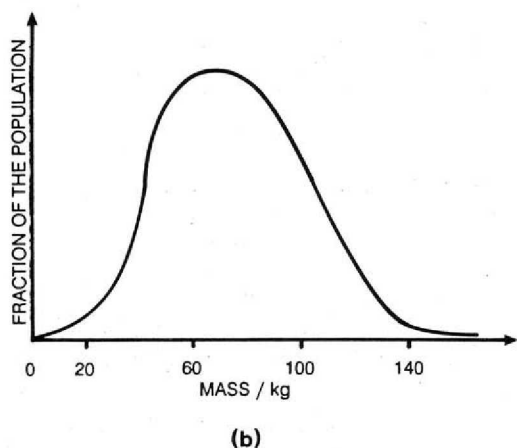
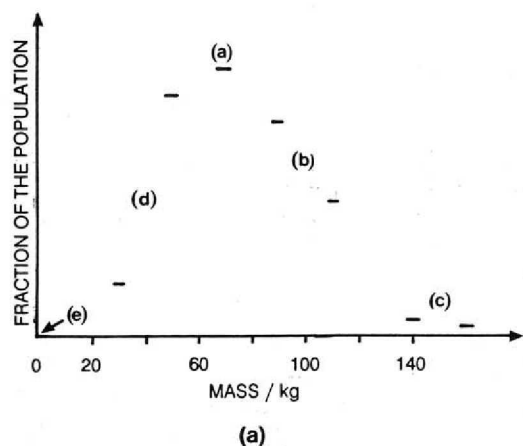


Figure 1. (a) Possible distribution of mass among 30-year-old men using a 10-kg range. (b) The corresponding distribution curve.

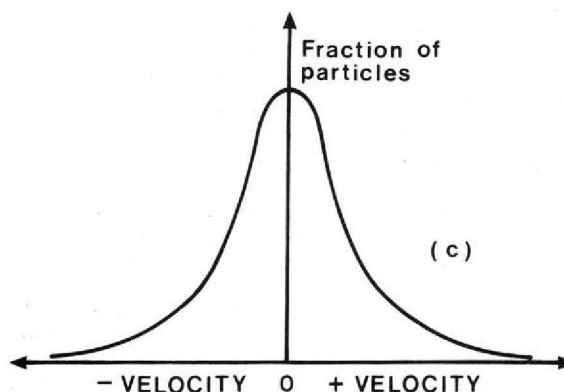
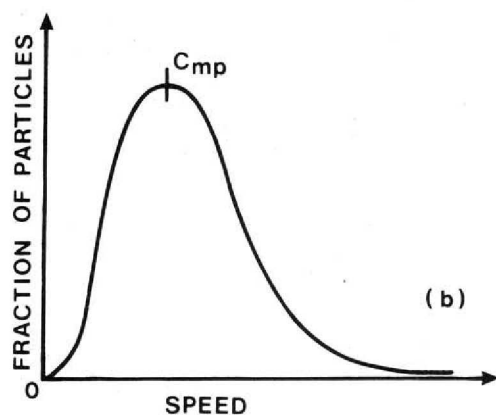
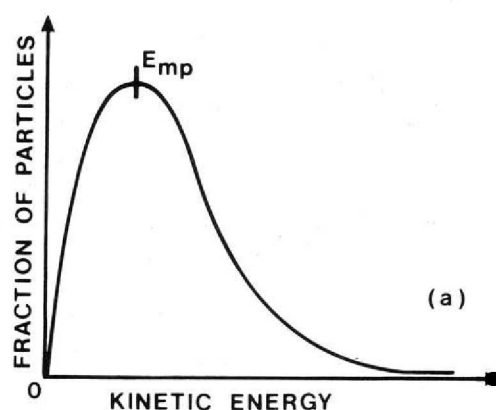


Figure 2. Maxwell-Boltzmann distribution diagrams. (a) Particle energies. (b) Particle speeds. (c) One-dimensional particle velocities.

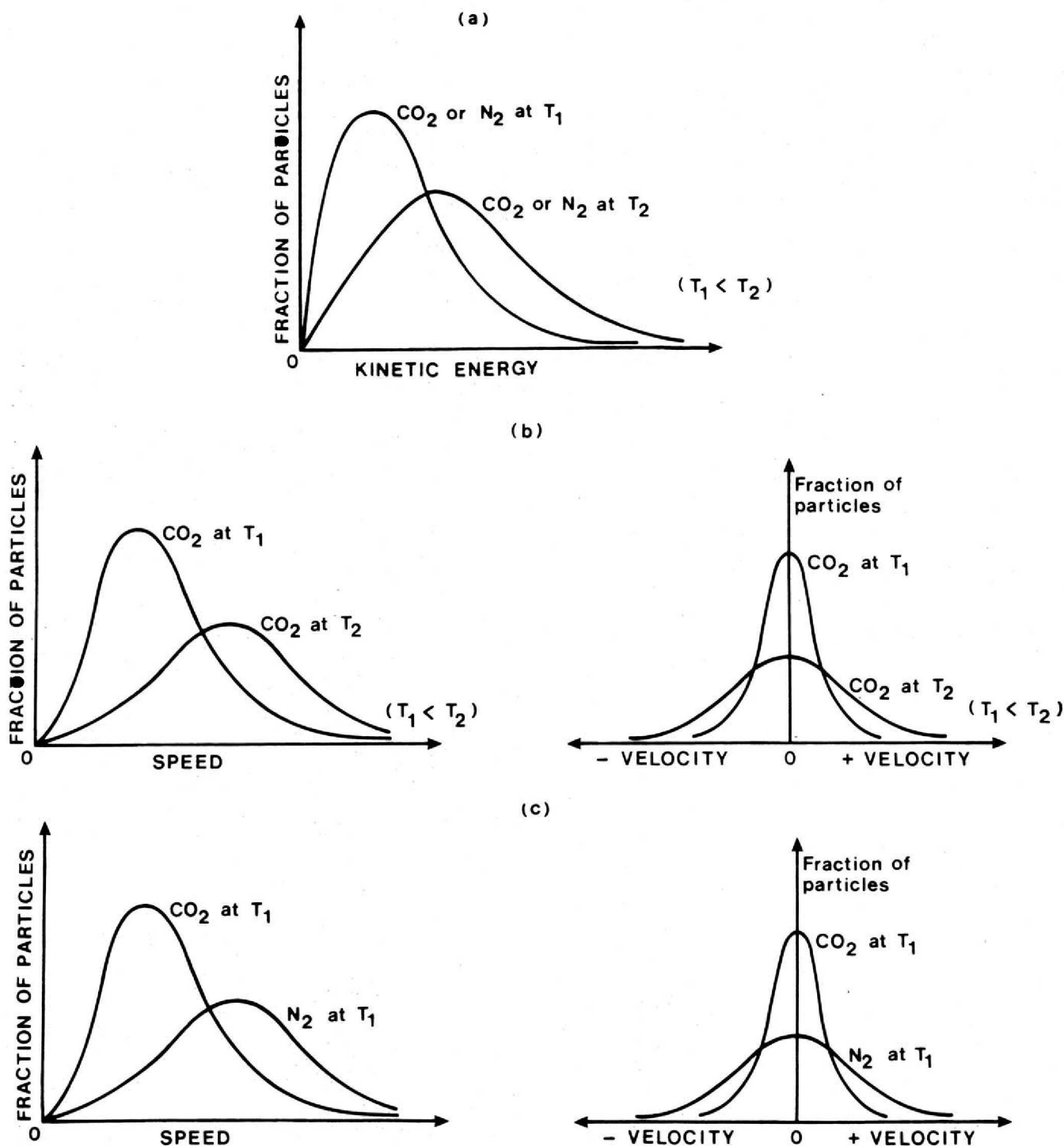


Figure 3. Various Maxwell-Boltzmann distribution diagrams. (a) Effect of temperature on the energy distribution. (b) Effect of temperature on the speed and velocity distributions. (c) Effect of particle mass on the speed and velocity distributions.

A Concrete Analogy

We believe that a qualitative explanation of the general shape of the curves should be given. Possibly one of the simplest ways to do this is to compare the distribution of kinetic energies in a collection of ideal gas particles with the distribution of mass among 30-year-old men in a particular population. (Although any argument by analogy will contain weaknesses, they are often a small price to pay for the improved initial understanding that is gained.)

If we plot the fraction of 30-year-old men in a given mass range as a function of mass, we would probably obtain a graph with the following characteristics (see Fig. 1a).

- A peak between about 65 kg and 75 kg because more men have a mass in this range than in any other range (region a of Fig. 1a).
- A decrease at higher masses because relatively few men are in the 85 to 95 kg range, and even fewer are in the 105 to 115 kg range (region b).
- An asymptotic approach to the x axis at high mass because we make the simplifying assumption that there is no theoretical limit to anyone's mass (region c).
- The graph would also decrease at lower masses because fewer people are in the 45 to 55 kg range, and fewer still in the 25 to 35 kg range (region d).
- Because a person cannot exist with zero mass, the graph will approach the origin, where it stops (region e).

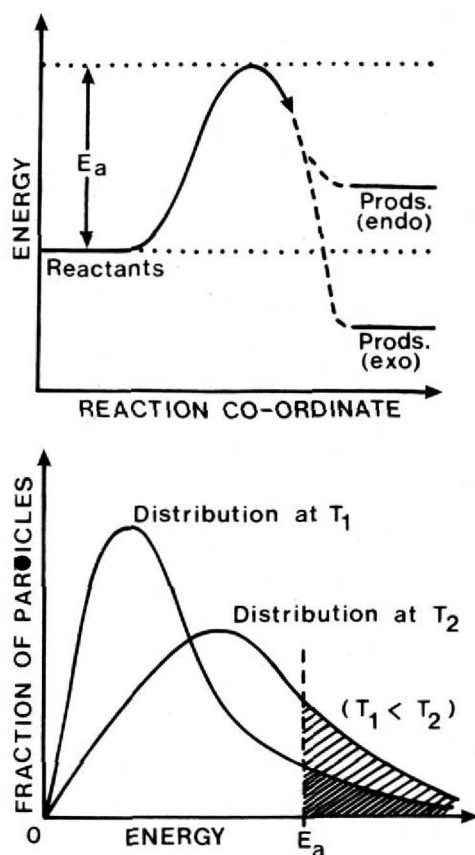


Figure 4. The effect of temperature on energy distribution and, thus, on reaction rates.

If the ranges are allowed to become infinitesimally small then the discrete graph (Fig. 1a) will become a continuous curve—the distribution curve (Fig. 1b).

Common Textbook Errors in Introducing the Concept

After introducing the distribution diagrams, textbooks should correctly depict the general qualitative features. However, a survey of reputable physical chemistry textbooks showed that the diagrams were often incorrect or misleading.¹

Typical errors include curves that do not go to the origin and curves that meet the x axis, rather than approaching it asymptotically at higher values of x . A surprisingly common error is to label the speed distribution, which is skewed, as the velocity distribution, which is symmetric.

However, the most common error is to show the initial portion of the energy distribution curve with an increasing (concave up) slope. This is correct for molecular speeds, but not for kinetic energies. Figure 2 may clarify the situation.

Comparing the Distribution Diagrams That Describe Molecular Behavior

The curve for the translational kinetic energy distribution is described by the following formula.

$$f(\epsilon) = 2\pi \left(\frac{1}{\pi kT} \right)^{3/2} \epsilon^{1/2} \exp \left(\frac{-\epsilon}{kT} \right) \quad \epsilon \geq 0 \quad (1)$$

For the speed distribution, the formula is

$$g(c) = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} c^2 \exp \left(\frac{-mc^2}{2kT} \right) \quad c \geq 0 \quad (2)$$

¹Details are available from the authors.

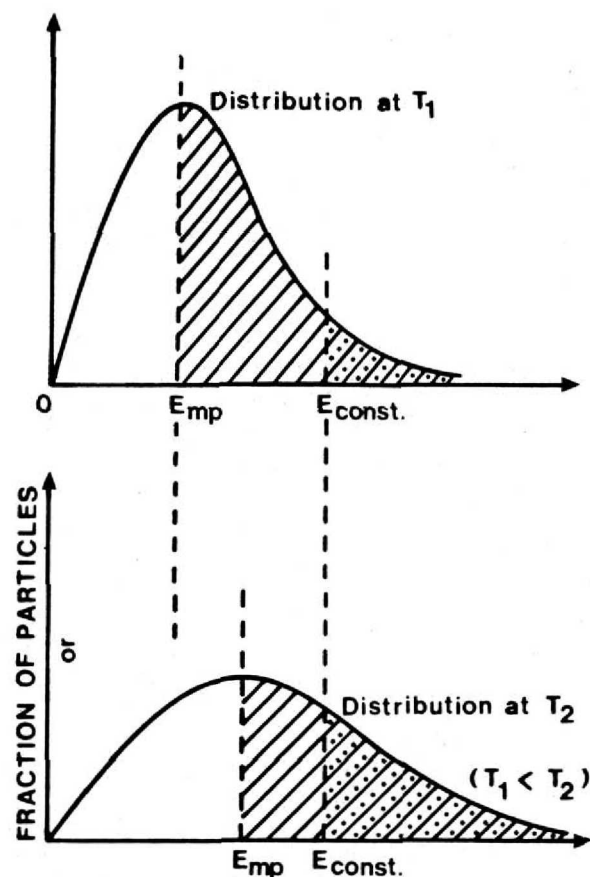


Figure 5. The effect of temperature on the fraction of particles with energies greater than the most probable energy E_{mp} and greater than a fixed energy E_{const} .

For the velocity distribution in the x direction, the formula is

$$h(v_x) = \left(\frac{m}{2\pi kT} \right)^{1/2} \exp \left(\frac{-m(v_x)^2}{2kT} \right) \quad -\infty \leq v_x \leq \infty \quad (3)$$

Plotting these equations yields curves of the general form shown in Figure 2.

The shapes of the speed and velocity distribution curves depend on both the temperature and the mass of the particle. (Equations 2 and 3 contain T and m .) In contrast, the shape of the energy distribution curve depends on the temperature only. (Equation 1 contains T but not m .) These effects are illustrated in Figure 3.

Juxtaposing Distribution Diagrams with Other Diagrams to Avoid Common Misconceptions

These distribution diagrams are very effective teaching aids. However, they are even more helpful when used with a diagram that illustrates the process that they are supposed to represent (1). This approach has been adopted by authors elsewhere (2) and may be applied equally well here.

The Effect of Temperature on Reaction Rates

For example, two curves that represent Maxwell-Boltzmann distributions are commonly drawn on one graph to show the effect of temperature on the rate of a chemical reaction. This type of graph is even more effective when used with a diagram that shows the potential energy changes that occur during the course of that chemical reac-

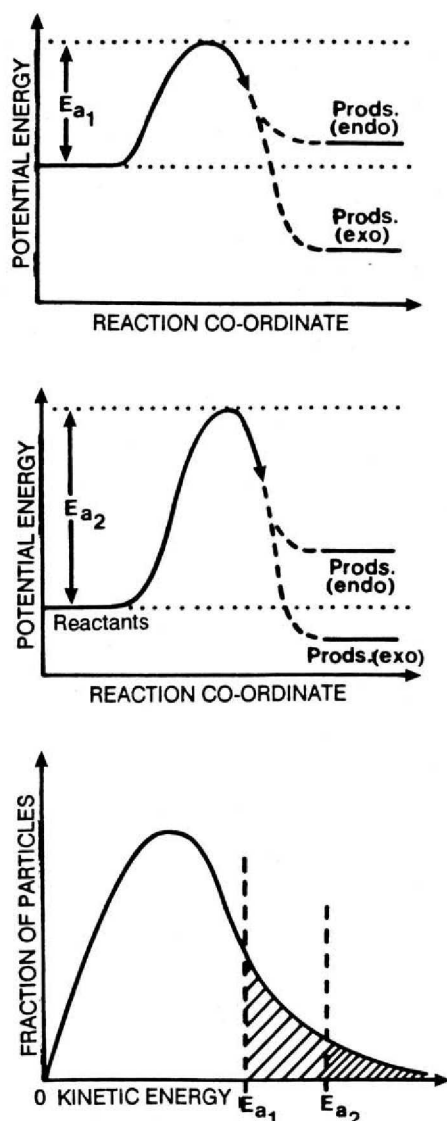


Figure 6. (a) The effect of activation energy on reaction rates for a reaction with a low activation energy. (b) The effect of activation energy on reaction rates for a reaction with a high activation energy. (c) The fraction of particles with energies greater than E_{a1} and E_{a2} .

tion. This is done in Figure 4. The activation energy E_a appears in both diagrams and clearly links them.

A particular advantage of Figure 4 is that it helps students who might otherwise confuse the effect temperature has on the rate of a chemical reaction with the effect it has on the position of a chemical equilibrium.

For example, when asked to discuss the effect of temperature on reaction rates, students often incorrectly argue that an endothermic process, which absorbs heat, will be speeded up by an increase in temperature, while an exothermic process, which releases heat, will be slowed down by an increase in temperature. Figure 4 helps to remove this misconception by showing clearly that an increase in temperature will increase the rate of any reaction, whether it is endothermic or exothermic.

Figure 4 also shows that an increase in temperature shifts the maximum in the energy distribution curve to higher energies while simultaneously flattening and broadening the curve. This broadening increases the fraction of particles with energies above a given fixed value.

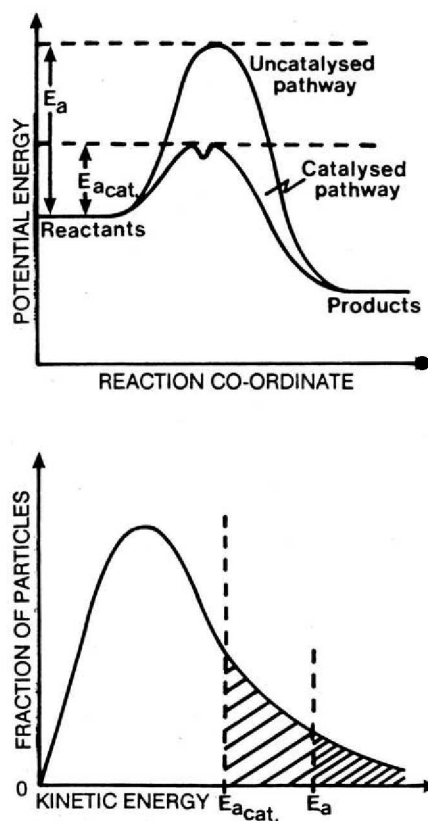


Figure 7. The effect of catalysis on reaction rates.

This broadening plays a major role in explaining the temperature dependence of reaction rates.

The Effect of Temperature on Various Phenomena

Contrary to common belief, the fraction of particles with an energy greater than the most probable energy does not increase with increasing temperature. That fraction is independent of temperature. This is illustrated in Figure 5, which shows that the fraction of particles with energies greater than the most probable energy is the same at both temperatures. In other words, the area shaded with solid lines is the same at both temperatures. On the other hand, the fraction of particles with energies greater than any particular fixed energy E_{const} is larger at the higher temperature. In other words, the area shaded with dotted lines is greater at the higher temperature.

The effect of temperature on the fraction of particles that have a kinetic energy exceeding some critical value is an important factor when considering the temperature dependence of a wide variety of phenomena, including the viscosity of liquids and rates of chemical reactions. These depend partly on the number of collisions in which the combined kinetic energy exceeds the threshold value of the activation energy. The use of the combined diagrams is particularly effective when discussing the effect of activation energy on the rate of a reaction.

The Effect of Activation Energy on Reaction Rates

Figure 6a shows the variation in potential energy for a reaction with a low activation energy E_{a1} , while Figure 6b shows a reaction with a higher activation energy E_{a2} . Figure 6c shows that even a small decrease in activation energy can lead to a large increase in the number of particles with an energy above the required value—provided the value of the activation energy lies in the right hand tail of the distribution curve.

Thus, other things being equal, the rate of a reaction with a low activation energy will be greater than the rate of a reaction with a high activation energy. If, on the other hand, the activation energy is so low that it lies in the left hand tail of the distribution, then the reaction is effectively instantaneous anyway, and it is largely insensitive to the magnitude of the activation energy.

The Meaning of Catalysis

In the same way, the effect of a catalyst on the rate of a chemical reaction can be seen in Figure 7. The catalyst provides a pathway with a lower activation energy. At fixed temperature this will increase the number of particles

with sufficient energy to react. Again, the occurrence of E_a and $E_{a,cat}$ in both diagrams provides a clear link.

Conclusions

We hope that we have demonstrated the wide usefulness of Maxwell-Boltzmann distribution diagrams, even at an elementary level. Hopefully many of the ideas and diagrams introduced in this article will find their way into future textbooks.

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the way, but once the final destination is reached, the change in enthalpy (altitude) is the same.

Depicting Energy Zeroes

Altitude also makes a good analogy for enthalpies of formation because both measurements are made relative to some value that is defined as zero:

- for defining altitude: sea level
- for defining enthalpies: the enthalpy of formation for elements in their naturally occurring forms at standard temperature and pressure

Using Disorder To Explain Entropy

Analogies related to entropy and disorder have also been published in *this Journal* (2, 3), and still others are found in various textbooks. In one example, entropy is compared to the way the student's room becomes messy—seemingly without effort—while tedious and deliberate work is required to straighten it (4).

An analogy that relates disorder to energy change is pictured in Figure 3. Energy is required to build something with blocks. However, after supplying a little activation energy, for example, by bumping into them, the blocks "spontaneously" fall into a more disordered state. The energy that went into the system to produce order is stored as potential energy in the blocks, and this energy must be lost when all the blocks are back on the floor.

In other words, disorder represents a more stable or probable situation because it minimizes the potential energy. (This may not be obvious in some phase changes unless one carefully defines the system and the surroundings. Check any good thermodynamics text.)

Larger copies of these illustrations, suitable for making overhead transparencies with a photocopier or thermofax, will be sent on request.

Acknowledgment

Thanks are due to Bruce Stiver of WSU Media Services for his talent in preparing the artwork and to the chemistry department for funding the preparation of these teaching aides.

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Heat and Work Are Not "Forms of Energy"

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College and university chemistry students are introduced, in varying degrees, to the rigors of thermodynamics. As a basis for these studies, definitions of the terms "heat", "work", and "energy" (among others) are required. A clear understanding of the restricted, thermodynamic definition of these three terms is complicated by the fact that they are already a part of the students' everyday vocabulary, where they are regularly and habitually used in a general and imprecise fashion.

For reasons that are partly historical, the terms tend to be loosely used, even among teachers and scientists and, therefore, attract a good deal of attention in educational journals (1–7). Although some textbooks (8–11) take care in presenting the concepts, others (12) sidestep the issue by introducing some of the terms, especially "heat", with no clear definition or discussion. However, some reputable texts (13–16) even perpetuate the fallacy that heat and work are "forms of energy".

The problem is further compounded by the fact that heat, work, and energy (in all its forms), can be measured using the same unit, namely the joule, and, therefore, it may seem reasonable to students that heat, work, and energy are all forms of the same thing.

Thermodynamically speaking, heat and work are not "forms of energy", but are *processes* by which the internal energy of a system is changed. They manifest themselves only at the boundary of the system and then only during the process of change.

At the macroscopic level, heat is the process of energy transfer as a result of a temperature difference, while work is the process of energy transfer as the result of a change in the external parameters that describe the system. At the microscopic level, the transfer of energy by heat leads to a redistribution of particles over unchanged energy levels, while the transfer of energy by work leads to a shift of some of the energy levels of the system.

These ideas may be introduced, even at high school level by the judicious replacement of the word "heat" (as a noun) with the word "energy". For example, no confusion would be caused when introducing calorimetry, by saying that "energy gained equals energy lost" in place of "heat gained equals heat lost."

When "heat" is used as a verb, in its various forms, no change is required as long as "heat" (as a verb), "heating", "heated", etc. are understood to mean that a particular process has been used to add energy to the system, and it is realized that the same amount of energy could have been added by various other processes.

An Analogy for How Heat and Work Differ from Energy

The following analogy helps to clarify the distinction. Imagine that energy is like money in the bank. Money, measured in dollars, may be deposited or withdrawn from your account by various means. These include the use of checks and the use of various electronic methods such as automatic teller machines, ATM's. Deposits or withdrawals made by check or by ATM's also are measured in dollars, but this does not mean that checks and ATM's are themselves forms of money. They are actually processes by which money is transferred to or from your account. Now, in the same way, heat and work are not themselves forms of energy, but are two different processes by which energy is transferred to or from a system.

Some students may argue that a check is in fact a form of money. If necessary, quick reference to any reputable dictionary will emphasize that a check is actually a set of written instructions, directing a banker to transfer a specific amount of money from a specified source to a specified destination. Should this misunderstanding regarding the meaning of the word "check" arise in class, it may itself be used as an analogy to illustrate how the word "heat" is commonly misunderstood.

The analogy may be extended by recognizing that check and ATM transactions may take different forms. Checks, for example, may be negotiable or non-negotiable. In the same way, work may be transferred in different forms—such as mechanical work or electrical work. Similarly, ATM transactions may take the form of cash withdrawals or the electronic transfer of money between various ac-

counts. By analogy, heat transfers may take place by conduction, convection, or radiation.

Explanations by analogy are fraught with weaknesses, particularly if they are extended too far or if they are examined in detail. Despite these weaknesses, the simplicity and clarity of a good analogy appeal to students and teachers alike. Furthermore, explanation by analogy rests on the sound pedagogic principle of adding to a student's existing knowledge and experience rather than trying to generate a new, isolated body of concepts.

In this context we have found the above analogy to be extremely effective in countering the misconception that heat and work are "forms of energy" when introducing our students to the mysteries of thermodynamics.

Acknowledgment

Constructive suggestions by the reviewers are acknowledged with appreciation.

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Phase Diagrams of One-Component Systems

What Most Textbooks Don't Say, but Should!

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The pressure-temperature phase diagrams of simple one-component systems form a part of most chemistry courses (1) both at high school and at undergraduate level. Thus, the topic is covered by a large number of reputable textbooks. It is surprising to find that many of them contain errors and omissions that have drawn little comment in educational journals (2, 3).

Figure 1 shows the way in which the P - T phase diagram for a one-component system is typically presented. The fact that the liquid/vapor equilibrium line terminates at a critical point is strongly emphasized in virtually every textbook. Despite this emphasis, both the diagrams and the accompanying explanations fail to give equal treatment to the other equilibrium lines that usually are drawn ending in the middle of nowhere (see Fig. 1). In fact, the solid/vapor line goes to the origin in all known cases except that of helium (4) (see Fig. 2) and the solid/liquid line has no known upper limit (5). It may be a good idea to emphasize this fact by ending the solid/liquid line with an arrow head or with a series of dots (see Fig. 2).

The vast majority of textbooks take care to indicate that the liquid/vapor equilibrium line cannot extend to regions above the critical temperature but fail to indicate that the solid/liquid equilibrium line is not restricted in this way and also extends above the critical temperature at very

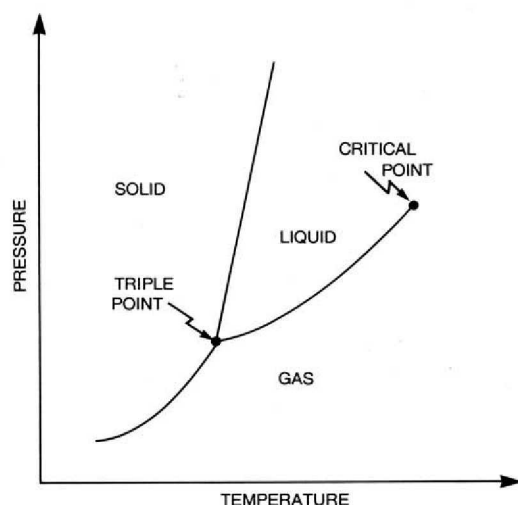


Figure 1. A simple phase diagram typical of those used in many textbooks.

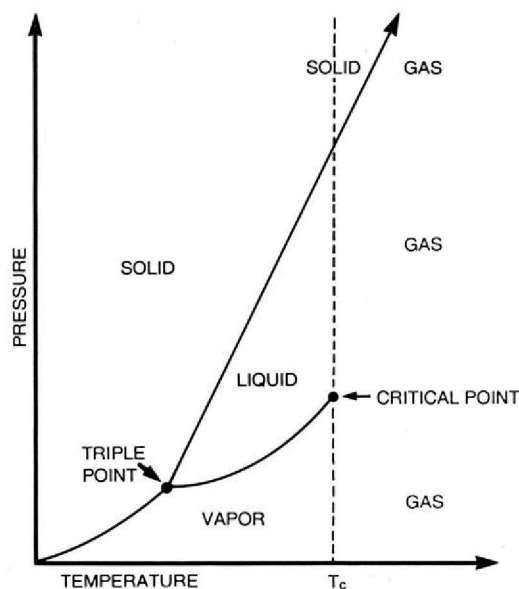


Figure 2. A better representation of a simple phase diagram.

high pressure (6). As a direct result of this omission, it is common for students to believe that only the gas phase can exist at temperatures above the critical temperature while in fact solid phases also will exist there at high pressures (See Figs. 2 and 3).

Attention often is drawn to the fact that several different solid phases may exist, each characterized by a different crystal structure (allotropy or polymorphism). The phase diagram of sulfur showing its rhombic and monoclinic forms is commonly used as an example. Having drawn attention to the possible existence of several *solid* phases, it might be expected that the liquid and vapor phases would receive similar attention. However, this is not the case, and it is rarely mentioned that for all known one-component systems there is only ever *one* vapor phase and *one* liquid phase except in the case of helium that is unique in having two liquid phases (7).

Specific reference should be made to the fact that the diagrams are not drawn to scale and that this is done deliberately in order to emphasize certain features that may not be apparent on a scale diagram. It may not be necessary to discuss these features, but for example, the important pos-

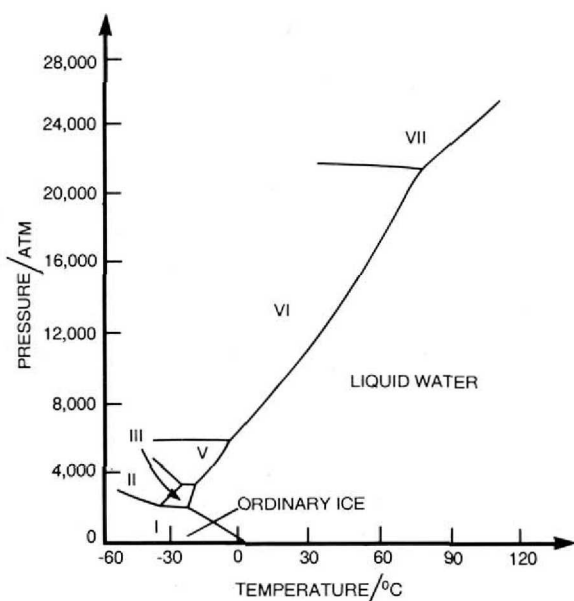


Figure 3. The phase diagram of water at high pressures.

itive or negative slope of the solid/liquid equilibrium line essentially would vanish and appear as a vertical line unless the scales were distorted. Also, for many systems, the solid vapor, and much of the liquid/vapor equilibrium lines would merge with the temperature axis on a linear scale drawing (see Fig. 3).

The problem of scales becomes especially apparent when the phase diagrams of carbon dioxide and water are drawn alongside each other, as they often are, with almost every detail the same and only the slope of the solid/liquid equilibrium line distinguishing between the two diagrams. This creates the false impression that the slope of the solid/liquid line is the only distinguishing feature between

the two systems. It is a useful exercise to ask students to draw sketch diagrams of the two systems on the same set of scaled axes after providing them with the relevant data.

Many texts fail to emphasize that these phase diagrams apply only to pure substances (one-component systems) and that the presence of any other substance, even something like air, may make a difference to the way the system behaves. Many of these differences may be small, such as the small difference between the normal melting point of pure water (0.002 °C) and that of air-saturated water (0.000 °C). However, failure to appreciate this point may lead the student into more serious misconceptions. For example the P - T phase diagram for water suggests correctly that ice will sublime only at pressures below about 0.006 bar, but students are likely to be puzzled by the fact that ice does, in fact, sublime in winter and in deep freezers at normal atmospheric pressures of around 1 bar, well above the upper limit suggested by the phase diagram. It is then necessary to explain that sublimation will occur only when the *partial* pressure of the water vapor in the two-component water/air system is below about 0.006 bar, although the *total* pressure is far above that of the triple point.

The typical general chemistry textbook for freshmen devotes an average of about three pages to a discussion of one-component phase diagrams. Their presentation and completeness could be enhanced significantly by the addition of just a few carefully worded sentences, and slight modifications to the accompanying diagrams, along the lines suggested in this article.

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First-Law Problem Solving

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The subtleties of physical chemistry in general and thermodynamics in particular have led to the introduction of various charts, mnemonics, algorithms, tables, etc., to help struggling students clarify their thinking (1-4). For many years we have used a chart like that proposed by Hamby (5). However, we have found that its usefulness was limited because students often failed to distinguish among many of the expressions.

For example, the following expressions

$$\Delta U = n\bar{C}_V\Delta T$$

and

$$\Delta H = n\bar{C}_P\Delta T$$

hold for isochoric, isobaric, and adiabatic processes involving ideal gases.

This often confuses the students. For example, students often believe that ΔU is the same for all three cases. The convention for writing the equations does not show that the ΔT term differs in each case. We have tried to clarify this in our scheme by using $\Delta T'$, $\Delta T''$, $\Delta T'''$, etc., and by asking our students to draw the appropriate P - V diagrams. Even this approach had only limited success until

we hit on the idea of combining and superimposing the various P - V diagrams as shown in the figure.

A Helpful Diagram

In this diagram it is assumed that an ideal gas is expanded from an initial state of P_2 , V_1 , T_3 (point 1) by various processes to a final pressure of P_1 . The diagram is constructed by

- qualitatively considering the work done by the gas as it expands
- considering the heat changes and their effect on the temperature of the system

For example, consider an adiabatic expansion against a constant pressure P_1 (point 1 to point 3 along the dashed line). Because the process is adiabatic, no heat exchanges occur with the surroundings. Thus, the work of expansion is done at the expense of the internal energy of the system, which must decrease.

However, for an ideal gas, the internal energy is proportional to the temperature. Thus, the temperature must also decrease, leading to a final temperature and volume at point 3. This final temperature and volume are lower than they would have been if expansion had occurred isothermally (point 1 to point 4 along the dashed line) because, in the isothermal case, the gas does not draw on its internal energy to provide the energy required to carry out the work of expansion. Instead it draws this energy from the surroundings by absorbing heat. Consequently, point 3 must lie to the left of point 4, that is, at a lower temperature. By a similar argument point 2 must lie to the left of point 3.

Interestingly, for an ideal gas, the expression

$$\Delta U = n\bar{C}_V\Delta T$$

will hold for both constant-volume and constant-pressure processes because the internal energy of an ideal gas depends on temperature only. Thus,

$$\left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_P = \bar{C}_V$$

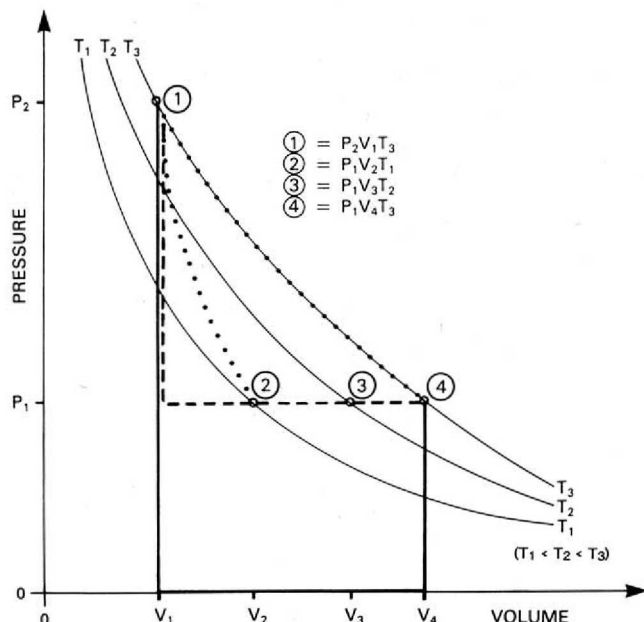
Similarly $\Delta H = n\bar{C}_P\Delta T$ both for isobaric and isochoric processes because

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_V = \bar{C}_P$$

The case of real gases is not quite so straightforward and is adequately described elsewhere (6).

Additional Exercises

The figure has been of great help to our students in visualizing the relationships and differences among the vari-



- ① → ④ Isothermal or adiabatic expansion against zero external pressure
- ① → ② Isothermal expansion against a constant external pressure, P_1
- ① → ③ Adiabatic expansion against a constant external pressure, P_1
- ① → ④ Reversible, isothermal expansion to P_1
- ① → ② Reversible, adiabatic expansion to P_1

The expansion of an ideal gas from P_2 to P_1 by various pathways.

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ous processes involving ideal gas expansions. Although the figure contains most of the basic processes that are typically considered in an undergraduate textbook, other processes could be added if necessary.

A particularly useful exercise is to get students to redraw the diagram, this time assuming that the ideal gas expands from an initial state of P_2, V_1, T_3 (point 1) to a final volume of V_4 by various processes. The resulting diagram looks like the figure, but the various final states do not lie at appropriate volumes along the P_1 isobar. Instead they lie at appropriate pressures along the V_4 isochore.

Summary

P - V diagrams of individual processes are widely used in thermodynamic textbooks but are rarely linked by super-

position. The problems that result from compartmentalizing the various thermodynamic processes have been indicated, and the use of superimposed P - V diagrams to clarify the issue has been suggested. Overall, the principle of combining P - V diagrams has much to recommend it.

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A New Use for the Candle and Tumbler Myth

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Several methods for determining the oxygen content of air as a percentage by volume have appeared in chemistry textbooks and in *this Journal* (1–3). Of these, the procedure suggested by Birk et al. (3) involving the rusting of steel wool is ideal for use by students as it meets the important criteria of being simple, rapid, accurate, and above all, safe. We have since adapted this method to incorporate the excellent suggestions made by Meek (4). The experiment involves a waiting period of about 30–60 min while the oxygen in the trapped air is consumed. We have found a productive way to use this time in a manner that is directly related to the main experiment.

Introducing the Bogus Experiment

During the waiting period students are asked to determine the percentage oxygen in air by a “quicker and simpler” method—this method being the old, bogus “candle under a tumbler” method. To our amazement this procedure is still finding its way into textbooks (5–7) as a supposedly valid method, despite having been thoroughly repudiated (8, 9).

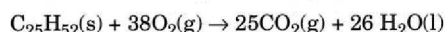
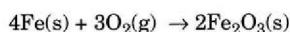
The method involves lowering an inverted beaker over a burning candle that is floating in a bowl of water. The apparent volume of oxygen trapped in the inverted beaker is determined from the extent to which the water rises in the beaker after the flame dies. The procedure takes only a minute or two to perform. Students are asked to repeat it several times and average the results.

We make use of 600-mL tall-form beakers and candles about 20 mm in diameter cut into disks about 15 mm high. This equipment usually gives volume changes of between 15% and 25%. Using candles cut into disks is not essential but has the advantage that the candle floats with the wick upright and does not need to be mounted on a holder.

The benefits of this bogus experiment become apparent when students fill out their result sheets. Having completed the calculations for the percentage oxygen by the two different methods, they are asked to give a brief comparison of the two methods. Students typically conclude that both methods are satisfactory and that the steel wool method is accurate, but slow and difficult, while the candle method may be less accurate but has the advantage of being quick and easy.

Using the Results to Enlighten Students

Students are then told that candle wax consists mainly of the hydrocarbon pentacosane, $C_{25}H_{52}$, and that rust may be represented reasonably by the formula Fe_2O_3 . With this information they are asked to write out balanced equations for the oxidation of iron and for the combustion of candle wax:



Students are asked to distinguish between the two reactions in terms of the volume of gas consumed relative to the volume of gas produced and are asked to think about the relative densities of hot and cold gases. They are then asked to re-evaluate the two methods. We end the session with a class discussion. The oxidation of steel wool has been discussed adequately in earlier references, but the

following aspects of the candle experiment have cropped up, sometimes spontaneously from the class and other times introduced by instructors to stimulate discussion.

Normal air contains about 21% oxygen by volume, and if all of this was used up and replaced by CO_2 then the appropriate equation shows that a volume change of about 7% would be expected:

$$((38 - 25)/38) \times 21\% = 7\%$$

This result could be tested by initially positioning the beaker just above the water and alongside the flame rather than above it. Rapidly moving the beaker over the flame and down into the water should trap a fixed volume of cold air that will then be heated up as the oxygen is supposedly consumed and replaced by CO_2 . On cooling back to room temperature a volume change of about 7% would support the speculative conclusions given above. However, when attempting to demonstrate this procedure, it is impossible to prevent large bubbles of hot air from escaping from the beaker, no matter how carefully or quickly it is plunged down into the water. These bubbles escape because the water pressure is too low to contain the expanding gases.

It is, thus, clear that the results of this procedure have little to do with the consumption of oxygen or the production of CO_2 , but are almost exclusively due to the contraction of the hot air trapped in the beaker. A Charles' Law calculation shows that the temperature of the hot air in the beaker must be about 90 °C in order to account for a 20% change in volume as the gas cools back to about 20 °C.

Most importantly, the oxygen is *not* totally consumed by the flame. Results show (8) that the final mixture still contains a substantial amount of oxygen that varies inconsistently from 15% to 19% by volume. Clearly, the flame is not extinguished by the total absence of oxygen but probably by rising levels of CO_2 and more importantly by the inefficient transport of the remaining oxygen to the flame.

Cooper (10) claims that the candle under a tumbler method is successful because all the CO_2 that is produced dissolves in the water, and thus the net change in volume is due only to the consumption of oxygen. The solubility of CO_2 is in fact sufficiently high (11), but even if it dissolves rapidly at ambient temperatures and pressures this will not obviate the problem of incomplete oxygen consumption discussed above. A demonstration using water that is saturated already with CO_2 produces no effect on the results of this experiment, thus further dispelling the CO_2 dissolution hypothesis.

The fact that fairly consistent results may be obtained with a specific procedure is simply an indication of the consistency of the procedure itself and has no bearing on the accuracy of the experiment. The fact that a particular combination of certain flame sizes, beaker sizes, and techniques may consistently produce a volume change of around 20% is purely a fortuitous combination of these and other variables. We have made an extended effort to find how the final volume change varies with flame size, beaker size, the method and rate of sealing the inverted beaker etc. This has been largely unsuccessful and has produced only one significant result. Candles mounted so that the flame is near the top of the inverted beaker are extin-

guished several seconds before those that are mounted near water level (floating).

Conclusion

Students usually are exposed only to well-tested experiments that always "work" and thus tend to accept the procedure and results without question. If well chosen, the occasional combination of "good" and "bad" experiments can be a powerful pedagogic tool and the value of this bogus experiment lies in showing students how easily we can be misled and how a little thought could prevent this.

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Basic Principles of Scale Reading

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From a junior school student using a ruler, to a pilot in a dial-crammed cockpit, the ability to read scales on an assortment of instruments is a basic survival skill in the modern world. This is especially true in the experimental work that forms an integral part of science education.

Despite the obvious need for scale reading skills we have failed to find a single textbook or laboratory manual that addresses the problem. Many texts mention the error of parallax and the use of vernier scales, but these are discussed in isolation, with no reference being made to the principles of scale reading in general. Elementary science texts appear to regard the topic as inappropriate, while more advanced texts apparently presume that the skill already has been mastered. As a result the basic principles of scale reading are not available in any literature that is readily accessible to the student or teacher.

If you need any convincing that many students have difficulty in reading scales, then ask them to record the readings shown in Figure 1. Figure 1(a) shows part of a buret scale, Figure 1(b) shows the scale of a voltmeter connected to the 15 V scale and Figure 1(c) is the scale of a polarimeter. Even at the end of their first semester, few undergraduates will read all three scales correctly as (a) 27.85 mL, (b) 11.4 V and (c) 2.65°. Even the simple buret scale in Figure 1(a) will be read as 28.15 mL by a significant number of students, while the voltmeter scale typically will be read as 12.8 V.

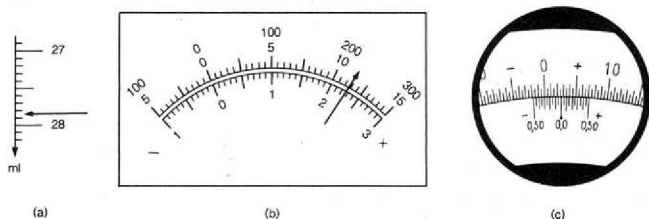


Figure 1. Typical instrument scales; (a) buret; (b) voltmeter; (c) polarimeter.

Although this article seeks to alleviate the problem, it is difficult to avoid using cumbersome verbal descriptions. Nevertheless, the use of numerical examples shows that the application of these descriptions is straightforward.

Terminology

The scale on an instrument usually consists of a line, straight or curved, divided into spaces that we shall call "scale units" by graduations that are numbered at regular intervals (Fig. 2). A reading on the scale is indicated by the position of a marker that may take the form of a pointer, meniscus etc.

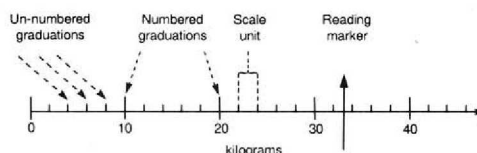


Figure 2. Numbered and unnumbered graduations on a scale.

Procedure

Step 1. Determine the Value of Each Scale Unit

To do this, subtract the value of any numbered graduation from the value of the next, larger numbered graduation. Divide this figure by the number of scale units that occur between the two numbered graduations. The same result will be obtained no matter which numbered graduations are chosen. Using Figure 2 as an example:

$$\frac{(30 \text{ kg} - 20 \text{ kg})}{(5 \text{ scale units})} = \frac{(10 \text{ kg})}{(5 \text{ scale units})} = 2 \text{ kg per scale unit}$$

Check: Start at, say the 20-kg graduation and then move toward the right-hand side, adding 2 kg for each scale unit. You should get to the 30-kg graduation on the scale after five additions.

Step 2. Determine the Value of the Closest Graduation on the Zero Side of the Marker

Using Figure 3 as an example, the scale units will be:

$$\frac{(3 \text{ kg} - 2 \text{ kg})}{(10 \text{ scale units})} = 0.1 \text{ kg per scale unit}$$

Now, the value of the graduation on the "zero side" of the marker will be the value of the closest, numbered graduation on that side (2 kg), plus the product of the number of complete scale units between this graduation and the pointer (3 scale units in this case), and the value of each scale unit (0.1 kg); i.e., $(2 \text{ kg}) + (3 \text{ scale units} \times 0.1 \text{ kg/scale unit}) = 2.3 \text{ kg}$

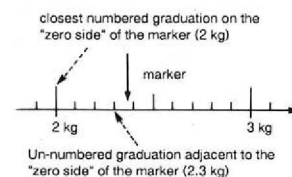


Figure 3. A reading that lies between two graduations.

Step 3. Estimate the Value of the Last Digit

Estimate the position of the marker within the scale unit as a decimal fraction of the scale unit as a whole. Using Figure 3 as an example we may estimate that the pointer is about seven tenths (0.7) of the way along the scale unit. This estimate is then multiplied by the value of the scale unit:

$$(0.7 \text{ scale units}) \times (0.1 \text{ kg per scale unit}) = 0.07 \text{ kg}$$

Other equally reliable observers may estimate that this value should be 0.06 kg or 0.08 kg and since this digit is already an estimate, it is clearly not possible to estimate any further digits, the important principal being that, "The first estimated digit also must be the last digit."

Step 4. Determine the Final Reading

The final reading is obtained by adding the results of steps 2 and 3:

$$2.3 \text{ kg} + 0.07 \text{ kg} = 2.37 \text{ kg}$$

(The rules pertaining to the use of significant figures have been ignored for the sake of simplicity.)

Because the final digit is only an estimate, there can be no absolutely "correct" reading, however, in the example from Figure 3, the final reading always will have two decimal places, and a reading of 2.3 kg (one decimal place) would not convey the inherent accuracy of the scale, while a reading of say, 2.375 kg (3 decimal places) would imply an accuracy beyond the limits of the scale.

As a rule of thumb, a reading may be estimated to one order of magnitude more than the order of magnitude of the scale unit. For example, in Figure 3, the scale units are tenths (10^{-1} ; one decimal place) of a kilogram, thus an estimate to hundredths (10^{-2} ; two decimal places) of a kilogram would be expected.

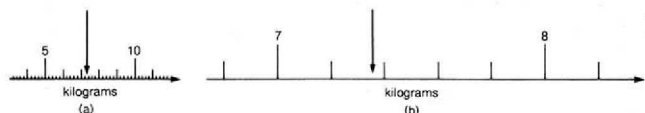


Figure 4. Scales with (a) closely spaced and (b) widely spaced graduations.

Despite the general usefulness of this simple approach, there are cases where either more or less decimal places may be appropriate. For example Figures 4(a) and 4(b) show two scales, both having scale units with a value of 0.2 kg and both having a reading somewhere between 7.2 kg and 7.4 kg. However, the scale in Figure 4(a) has closely spaced graduations and a reading of 7.3 kg (one decimal place) would be acceptable. By contrast, in Figure 4(b) the graduations are much more widely spaced and a reading of 7.35 kg (two decimal places) would be preferred. It is clear from this example that there can be no specific spacing at which one changes from a reading with one decimal place to a reading with two decimal places, but also it is clear that two decimal places would be excessive in the case of Figure 4(a) and that one decimal place is inadequate in the case of Figure 4(b).

Readings that Coincide Exactly with a Graduation

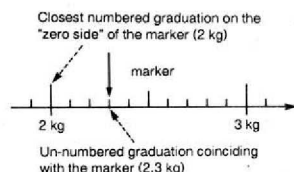


Figure 5. A reading that coincides exactly with a graduation.

The examples used above assumed that the reading lay between two graduations. However, it occasionally is possible that the marker appears to lie exactly on a graduation. In this case, record the value of this graduation and add a zero to indicate your estimation that the reading coincides exactly

with the graduation (see Fig. 5). In all cases, the last digit (and only the last digit) in each reading should be an estimated figure and so in this case 2.30 kg is an appropriate reading, while 2.3 kg or 2.300 kg are unacceptable for the reasons given above.

Problems with Estimating the Last Digit

Scales that have closely spaced graduations, may cause students some difficulty in estimating the final digit. Burets and rulers marked in millimeters are typical examples. Even in such cases it is possible for the inexperienced user to decide whether the reading appears to lie ON a graduation or BETWEEN two of the closely spaced graduations.

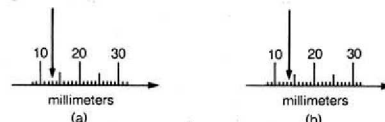


Figure 6. Scales with closely spaced graduations.

This distinction enables the crude estimate of a further digit, namely "0" if the reading appears to be on a graduation and "5" if the reading appears to lie between two graduation lines. Using Figure 6 as an example, marker (a) indicates a reading of 13.0 mm while marker (b) indicates a reading of 13.5 mm. With experience it becomes possible to make better estimates for the last digit.

Discussion

Instruments with digital displays are becoming increasingly common. If digital displays were going to replace conventional scales in the same way that the pocket calculator has replaced the slide rule, then the ability to read scales soon would become an unnecessary and obsolete skill. However, many simple and common instruments probably will retain conventional scales indefinitely and so the ability to read these scales is a skill that will be of value for the foreseeable future.

I regard the problem as serious enough to devote part of my first laboratory session with freshman students to scale reading. During this session a wide selection of instruments is set out. Students take the readings on each instrument and compare their result with the "correct" reading that is available on a card that is kept upside down next to the instrument. If, after taking a reading, a student finds that it is not correct when compared with that on the card, and if he or she cannot work out how the "correct" reading was obtained, then instructors are available to assist. Should logistics be a problem, the laboratory approach can be replaced easily or supplemented by using diagrams of the scales instead of the actual instruments themselves.

Conclusion

Teaching scale reading skills at an early stage saves a great deal of time and frustration for both students and staff in subsequent lab sessions.

Acknowledgment

The constructive suggestions of Clare T. Fuse are appreciated.

Exponential Notation

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Background

Typing exponential notation in the conventional form is tedious and space consuming and the results may be difficult to read. Other forms of notation have been proposed and are occasionally used, but none have yet gained wide acceptance or the sanction of a reputable scientific body. Consider the fraction

$$\frac{2.365 \times 10^{-4} \times 4.7 \times 10^{-2}}{5.80 \times 10^{-3} \times 8.6315 \times 10^{+7}} = 2.2 \times 10^{-3}$$

This is written much more compactly in the following form, which is often used in computer languages:

$$\frac{2.365\text{E} + 4 \times 4.7\text{E} - 2}{5.80\text{E} - 3 \times 8.6315\text{E} + 7} = 2.2\text{E} - 3$$

An even more succinct and elegant form has been suggested by Freeman (1) and was used by him in the "Reports" section of the *Bulletin of Chemical Thermodynamics* since the beginning of his editorship (2), as well as by Atkins (3, 4):

$$\frac{2.365\text{P}4 \times 4.7\text{N}2}{5.80\text{N}3 \times 8.6315\text{P}7} = 2.2\text{N}3$$

where $\text{XPY} = \text{X} \times 10^{+Y}$ and $\text{XNY} = \text{X} \times 10^{-Y}$

With the P/N notation it may be somewhat difficult to tell at a quick glance, where the mantissa ends and where the exponent begins. This may be improved by using lower case letters:

$$\frac{2.365\text{p}4 \times 4.7\text{n}2}{5.80\text{n}3 \times 8.6315\text{p}7} = 2.2\text{n}3$$

This p/n notation has several advantages and deserves serious consideration as a possible standard format.

Advantages

1. **Ease of Use.** To type: " $\times 10^{+x}$ " on most word processors requires about 12 keystrokes, depending on the change of fonts for the product sign and the exponent. Alternatively, a special macro may be created. Involving such a macro still requires several keystrokes plus the insertion of the relevant exponent. The p/n notation requires only a single keystroke plus the relevant exponent.
2. **Space Saving.** When the conventional notation is used within the body of a text, in calculations, or in tables of data, a larger line spacing is required to avoid the possibility that the superscripted exponents in one line will impinge on the subscripts or on the "tails" of characters such as "g, j, q, p" in the line above. This problem does not occur with the p/n notation, in which there can be no overlapping between lines, even with standard line spacing.
3. **Legibility.** Exponents in the conventional notation are usually typed in a very small font. In some cases this may be difficult to read. A 5 may look like 6

and 6 may look like 8 etc., especially when the paper or print quality is somewhat less than the best. This problem is particularly common when documents are photocopied, but is absent with the p/n notation, in which the same font is used throughout.

4. **Association.** Many widely used symbols are associated with the word for the corresponding quantity only in their language of origin. For example, the Helmholtz free energy is represented by the letter A, which apparently stands for the German word for work, namely "Arbeit". Other widely used symbols have no obvious link with the corresponding quantity in any modern language—for example, μ for chemical potential. However, p and n may be associated with the initial letter of the words "positive" and "negative" in most of the widely spoken languages of Europe and the Americas. This mental association, in conjunction with the advantages mentioned above, makes the p/n notation relatively "user friendly".
5. **Aesthetics.** The p/n notation is simpler, neater, more elegant and generally aesthetically more appealing.

Disadvantages

1. The p/n notation is unfamiliar to most people and so, initially, it may not be quickly and easily converted into the correct "mental image" of the number it represents (i.e., at first one may have to look at each number and "interpret" what it means). This situation is similar to the difficulties experienced some years ago by people converting from analog to digital watches. Often a period of adjustment is necessary before people can become accustomed to using a new (and better?) system.
2. The p/n notation breaks away from an established convention that has a long and ingrained tradition. Thus it can be expected that there will be a resistance, or rather an inertia, to its acceptance, despite its many advantages.

These disadvantages exist merely in the minds of users and should not be allowed to cloud the very real and tangible advantages of a better system of notation that deserves support and some form of official sanction.

Any doubts about the usefulness of the proposed p/n notation may be dispelled by considering the pH scale, which is a very telling chemical analogy. We are quite happy to write $\text{pH} = 3$ when what we really mean is $-\log_{10} [\text{H}^+] = 3$. The validity of any criticism of the p/n notation might well be tested by considering whether the pH notation would have stood up to a similar criticism when it was first proposed. The pH notation has all the advantages listed above for the p/n notation. All the p/n notation lacks is the acceptability that is gained through the familiarity of constant usage.

Finally, from a practical point of view, we were so impressed with the P/N notation when we first saw it, that we have used it in the modified p/n form with all our notes, exam papers, and data sheets ever since. Our

students have taken to the notation quite easily and it has become second nature to them. The use of this notation by authors and publications of the caliber of those mentioned in the literature cited lends substantial credibility to the new notation. If teachers, instructors, researchers, and publishers start using it unilaterally and widely, then official sanction will not be far behind.

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Vapor Pressure Lowering by Nonvolatile Solutes

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The vapor pressure lowering (VPL) that results when a nonvolatile solute is added to a solvent is a topic covered in virtually all freshman chemistry textbooks. That this phenomenon occurs is an experimental fact. However, contrary to the impression given in most texts, VPL seldom occurs in accordance with Raoult's law. In fact it has been strongly argued by Hawkes (1), that this "law" has little practical application and should be omitted from introductory chemistry courses.

Explanations offered for the phenomenon of VPL are inevitably wrong or, at the best, misleading. The VPL caused by addition of a nonvolatile solute brings about a reduction in the rate of evaporation of the solvent that will lead, via the liquid-vapor equilibrium, to a reduced vapor pressure. The fundamental error perpetuated in numerous chemistry texts is to attribute the reduced rate of evaporation to the occupation and consequent "blocking" of surface sites by nonvolatile particles. These texts typically argue that nonvolatile particles in the solution surface will block some solvent molecules from escaping to the vapor phase but will not impede vapor molecules that are condensing back into the solution. Some texts go so far as to support this incorrect explanation with detailed diagrams (2).

At an elementary level the blocked surface site theory may be easily dismissed by considering the following simple experiment. Float a few corks on the surface of a liquid. Surface sites will certainly be blocked, but the vapor pressure will obviously remain unaltered.

The alarmingly widespread occurrence of the fallacious "blocked surface sites" theory was noted by Mysels (3) as long ago as 1955. Although he supplied a comprehensive list of reasons for the incorrectness of the blocked surface sites theory, he offered no alternative explanation. Since then, this and other erroneous explanations have proliferated rather than vanished. As a result, it is necessary once again to bring the matter to the attention of educators and writers in the field of introductory chemistry.

Despite its extensive use, the blocked surface site theory is not the only incorrect explanation used to explain VPL. A less common but still erroneous explanation is illustrated by the following example: "Owing to the extra attraction that the water molecules feel for the dissolved particles, they find it harder to escape from a solution than from pure water" (4). Unfortunately, this simple and attractive explanation is also wrong. The molecular origin of VPL is not found in the energy of interaction between the solvent and solute particles. Ideal solutions, for which the solution enthalpy is zero, as well as solutions that form endothermically or exothermically, all produce a VPL that is independent of both the sign and the magnitude of the solution enthalpy.

Since vapor pressure lowering is not a result of enthalpy effects, it must then be a result of entropy effects (5). We have

found only one freshman chemistry text (6) that gives an adequate explanation of VPL by making use of a simple entropy-based argument. This is an approach that teachers and authors of future textbooks would do well to emulate. It is outlined very briefly below.

A solution is more "disordered" than a pure solvent. Thus the entropy difference between a pure solvent and its vapor will be greater than the entropy difference between a solution and its vapor. As a result, solvent molecules will have a greater tendency to leave the pure solvent than they do to leave the solution and the solution will have a lower vapor pressure. It will be noted that this simple explanation has nothing whatever to do with the blocking of surface sites by nonvolatile particles or with the energy of interaction between solute and solvent particles, and also avoids each of the objections raised by Mysels (3).

At a nonmolecular level, vapor pressure lowering may be correctly explained in terms of the chemical potentials, μ , of the pure solvent and the solution (7). However, this approach is generally beyond the level of the average chemistry freshman.

If students are not familiar with the basic concepts of entropy, then no attempt should be made to explain VPL. It should simply be stated as an experimentally verifiable fact. No explanation at all is better than a faulty one. We don't, for example, try to explain to freshmen why opposite charges attract each other. We simply note this phenomenon as an experimentally observable fact and leave it at that.

Comment

In the above discussion, when referring to entropy, the word "disordered" is used in quotation marks. This is done because the linking of entropy to molecular disorder may produce significant misconceptions. This has been discussed in numerous articles, of which the one by Lowe (8) is of particular excellence.

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The Electromotive Series and Other Non-Absolute Scales

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Science students encounter several common parameters for which absolute values are not, and in some cases cannot be, determined. These parameters include the Fahrenheit and Celsius temperature scales, potential energies, electrode potentials, and formation and reaction enthalpies. Handling these parameters is usually approached in the same way: a reference state is arbitrarily chosen and assigned some fixed and arbitrary value, which is usually, but not always, zero. Values of the parameter are then determined by measuring differences between a chosen state and the reference state.

Our experience has been that students generally have a limited understanding of this approach. Any doubts that may arise about the arbitrary selection of reference states and zero values are soon dispelled when they find that the unquestioned use of the approach leads to favorable grades. This lack of insight on the part of students is rarely apparent to instructors, possibly because they invariably question students only on the applications of such parameters. Instructors who doubt the validity of these assertions should try asking their students questions of the following type:

"In principle, could any electrode other than the hydrogen electrode have been chosen as the standard reference electrode? Explain your answer."

"In principle, could the standard hydrogen electrode have been assigned any value other than zero volts? Explain your answer."

"Imagine a table of E° values based on a standard Ag/Ag^+ electrode with an arbitrary E° value of 100 V. What would be the emf of the standard Daniell Zn/Cu cell on this scale? Explain your answer."

If we can, just once, give our students a clear understanding of the validity of this reference-state approach, it will stand them in good stead when it is used in subsequent sections of the syllabus. We find the following analogy to be particularly useful and we use it when introducing students to the electromotive series of electrode potentials.

Instead of a voltmeter, we use an "age meter". This imaginary instrument consists of a large, colorful cardboard cutout that looks like a voltmeter except that the units have been changed from volts to years. The scale

has a central zero with negative values on the left and positive values on the right. The age meter has a large movable pointer and comes complete with red and black wires terminating in large plastic crocodile (alligator) clips. The cardboard age meter is not essential to the success of the analogy, but it does add visual impact. When we first used this method the instructor personally acted as the age meter: hands = crocodile clips; arms = wires; body = meter; voice = output/reading.

We assume that the age meter, like the voltmeter, cannot measure the actual age of a student. It can only be connected between two students and used to measure the difference between their ages. Next we assume that the ages of all students in the class are unknown. Now if we knew the age of any *one* student, we could determine the ages of all other students by using our age meter to measure the difference between their (unknown) age and that of the student of known age.

But we do not know the age of any student. To bypass this problem we ask the class to arbitrarily select a "standard reference student" from their ranks. Next we use our age meter to theatrically measure the difference between the age of the reference student and the ages of several nearby students, moving the pointer on the age meter and assigning them values of +2 years, -3 years, +1 year, etc. The names and age differences are recorded on a table drawn on an overhead projector transparency (Table 1). To complete column 1 we assign

Table 1. Data from Hypothetical "Age Meter"

	1	2	3	4
Student	Age if $x = ?$	Age if $x = 0$	Age if $x = 12$	True Age $x = 16$
:	:	:	:	:
Sally	$x - 3$	-3	9	13
Brian	$x - 2$	-2	10	14
Jane	$x - 1$	-1	11	15
Reference student	x	0	12	16
Bill	$x + 1$	+1	13	17
Judy	$x + 2$	+2	14	18
:	:	:	:	:

the reference student an age of x years and then add names above or below the reference student in the appropriate places as indicated by the imaginary readings on our age meter.

Next we tell our students that just as zero volts was chosen as the potential of the SHE, we are going to choose zero years as the age of our reference student. This usually produces some chuckles, but we press on regardless and complete column 2 on the basis of our “zero age” assumption. Because the students did not seem to like our choice of zero as the age of the reference student, we offer to select a more realistic age. If the reference student appears to be about 16 years old, for example, we choose another reference age—one that is more realistic than zero, but still obviously wrong, say 12 years. This brings howls of protest from the class, but we remind them that we have no way of measuring the true age of the reference student and we are simply humoring their request for a more “realistic” value than zero. Column 3 is then completed on the assumption that $x = 12$.

Next, we tell the students that our fairy godmother knows the true ages of all the students, which she lists using invisible ink in column 4. This column will then contain “true”, or absolute, information that is not available to mere mortals.

It is only in the final step that students really begin to make sense of this analogy. In this step we discuss the usefulness of the data in each column. Obviously the data in column 4 would be the ideal choice, but we have no access to this information and so we must make the next best choice. When asked to choose the most useful column of data from columns 1, 2, and 3, students will generally opt for column 3 as being the best of a bad lot.

We point out that so far our procedure with the age meter has enabled us to make some significant progress. We have been able to correctly list all students in the order of their true age, with the youngest at the top of the list and the oldest at the bottom. Having done this we can do two more things: (i) for any pair of students, we can always tell which is the older, and (ii) for any pair of students we can always calculate the true numerical *difference* between their ages. For example, using the data for Bill and Brian from column 1:

$$(x + 1) > (x - 2) \therefore \text{Bill is older than Brian}$$

and the difference in their ages is

$$(\text{Bill's age}) - (\text{Brian's age}) = (x + 1) - (x - 2) = 3 \text{ years}$$

By applying the same process to the data in columns 2 and 3, we obtain exactly the same results in each case. We can also see that these results are exactly the same as those we would get from the true data in column 4, if only we had access to it.

We may conclude that as long as we restrict ourselves to differences in age, we do not need to know the true age of the reference student. Furthermore, we can assume any age we like for the reference age of the reference student— x , zero, and 12 have all been used, with equal success.

Is any of these columns of data (excluding column 4) better than the others? Well, the list in column 1 is cumbersome because of all the x 's, so columns 2 and 3 are probably more useful. These columns are similar, but column 2 has a slight advantage: we know that (i) true ages (as distinct from relative ages) cannot be negative, and (ii) our reference student is definitely *not* zero years old; so the use of the data in column 2 will constantly remind us that they are not absolute data, and that they are all relative to the chosen age of the reference student. By contrast, if we use the data from column 3, we may easily be lulled into believing that we are working with true and absolute data.

For this reason, column 2 gets the nod, and our arbitrarily selected reference student is assigned an age of exactly zero years, just as the SHE is assigned a potential of exactly zero volts, with all other electrode potentials being measured relative to this arbitrarily chosen value.

This particular analogy may be extended with some artifice. Let us presume that an older, stronger child can forcibly remove a packet of sweets from a second younger, weaker child, who is before her or him on our age list. The first child can in turn have the packet of sweets removed by a third older and even stronger child who comes after on our age list. In no case can a younger, weaker child forcibly remove sweets from an older, stronger child.

In the same way, a half reaction or electrode can remove electrons (be reduced) from any electrode that is above it in the electromotive series, but can in turn have its own electrons removed (be oxidized) by any electrode that is below it in the electromotive series. In no case can the reverse process occur. If you really want to push this analogy to its limits, then the number of sweets (electrons) gained by the older child must equal the number of sweets lost by the younger child!

If well planned, this analogy requires only 10 to 15 minutes of classroom time. It helps students gain insight and become aware of the validity of the procedure used to establish the electromotive series. It also clearly reinforces the fact that individual electrode potentials are only relative values, but any *difference* between these values is absolute.

The rewards of the analogy go beyond an acceptance and understanding of the basis of electromotive series because, as suggested in the opening paragraph, similar principles apply to a variety of other topics encountered by science students.

The Extent of Reaction, $\Delta\xi$ —Some Nuts and Bolts

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The concept of the “extent of reaction” was first formulated more than 80 years ago. Since then it has undergone regular refinements and modifications. The chronology of this development was presented by Dumon et al. (1), who referred to the multiplicity of concepts, symbols, and terminology that have been used to describe the extent of a chemical reaction.

Currently, the most widely used form of the extent of reaction is that which has been recommended by IUPAC (2). According to IUPAC the approved symbol for the extent of reaction is $\Delta\xi$ and the names “extent of reaction” and “advancement” are equally acceptable. For a particular chemical reaction involving a substance B, the extent of reaction is defined by IUPAC as

$$\Delta\xi = \Delta n_B / \nu_B$$

where $\Delta n_B = n_{f,B} - n_{i,B}$ ($n_{i,B}$ and $n_{f,B}$ represent the initial and final amounts of substance B, respectively) and ν_B is the stoichiometric coefficient of substance B. It is negative if B is a reactant and positive if B is a product.

From the definition of $\Delta\xi$ given above, it is clear that $\Delta\xi$ is an extensive quantity that has units of moles.

Garst (3) made some useful suggestions about how the extent of reaction could be used as a unifying basis for stoichiometry and showed how the usefulness of this concept may be profitably extended to elementary levels of chemistry. However, the extent of reaction, $\Delta\xi$, is more widely used in textbooks of physical chemistry, particularly in the sections that deal with free energy, chemical equilibrium, and kinetics. In earlier texts, sketch graphs of G versus $\Delta\xi$ were typically labeled with the independent variable, $\Delta\xi$, ranging from its minimum value of zero to a maximum value of one (4). Of course, this is not necessarily correct, since the definition of $\Delta\xi$ has no theoretical upper limit. In recognition of this fact, some highly reputable texts have recently changed their sketch graphs to leave the $\Delta\xi$ axis open ended (5). It is clear from this lack of consistency that the use of $\Delta\xi$ is still somewhat woolly.

From a pedagogical point of view, there is something elegantly satisfying about having the extent of reaction range from zero at the start of the reaction to a maximum value of exactly one, provided that the reaction goes to completion. If the upper limit were known to be one, then $\Delta\xi = 0.9$, for example, clearly indicates that the reaction is 90% of the way to completion and most of the reactants have been converted into products. If, however, we report that $\Delta\xi = 0.9$ without knowing the value of the upper limit, then, although we know the “amount of reaction” that has taken place, the fraction of reactants that has been converted into products is not obvious without further computation.

From a graphical point of view, having $\Delta\xi$ vary over a fixed range from 0 to 1 along the x axis allows one to draw a vertical y axis at $x = 0$ and another at $x = 1$. The y axis on the left may then be associated with pure reactants at the start of the reaction, and that on the right may be associated with pure products at the completion of the reaction. A further benefit of the 0 to 1 range is that it forms a close parallel with the way in which mole fractions are used, particularly as in the case of two-component phase diagrams.

The problem then, is to retain the convenient 0 to 1 range for $\Delta\xi$ without transgressing the requirements of IUPAC. This can be most easily achieved by first understanding how values of $\Delta\xi$ are influenced by (i) the way in which the chemical equation is written, (ii) the effect of differing initial amounts of reactants and products, and (iii) the role of a limiting reagent.

These effects may be easily understood by using a few simple numerical examples. For convenience we shall use examples involving the well-known Haber process, $N_2 + 3H_2 = 2NH_3$. For consistency, an arbitrary value of 15 moles will be used as the initial amount (n_i) of reactants and products wherever possible.

Example 1

At any given stage of a reaction, $\Delta\xi$ is the same for all reactants and products.

	$N_2 + 3H_2 = 2NH_3$		
ν	-1	-3	+2
n_i/mol	15	15	15

After the consumption of 2 mol of N_2 :

n_f/mol	13	9	19
$\Delta n/\text{mol}$	-2	-6	+4
$\Delta\xi/\text{mol}$	2	2	2

After the consumption of 4 mol of N_2 :

n_f/mol	11	3	23
$\Delta n/\text{mol}$	-4	-12	+8
$\Delta\xi/\text{mol}$	4	4	4

Example 2

Even when the initial and final amounts of reactants and products are fixed, the value of $\Delta\xi$ may vary in a way that depends on how the corresponding equation is written. This variation in $\Delta\xi$ results from the changes that occur when the stoichiometric coefficients, ν , are altered.

	$\frac{1}{2}\text{N}_2 + \frac{1}{2}\text{H}_2 = \text{NH}_3$			$\text{N}_2 + 3\text{H}_2 = 2\text{NH}_3$			$2\text{N}_2 + 6\text{H}_2 = 4\text{NH}_3$		
ν	$-\frac{1}{2}$	$-\frac{1}{2}$	+1	-1	-3	+2	-2	-6	+4
n_i/mol	15	15	15	15	15	15	15	15	15
n_f/mol	13	9	19	13	9	19	13	9	19
$\Delta n/\text{mol}$	-2	-6	+4	-2	-6	+4	-2	-6	+4
$\Delta\xi/\text{mol}$	4	4	4	2	2	2	1	1	1

Example 3

In cases where nonstoichiometric amounts of reactants and products are used, the maximum value of $\Delta\xi$ will be achieved when all the limiting reactant (LR) has been used up. This maximum value, $\Delta\xi_{\text{max}}$, is given by $\Delta\xi_{\text{max}} = -n_{\text{LR}}/\nu_{\text{LR}}$ and not by n_{LR} as has been reported (6). This is illustrated below and in example 4.

	$\text{N}_2 + 3\text{H}_2 = 2\text{NH}_3$			$\text{N}_2 + 3\text{H}_2 = 2\text{NH}_3$		
ν	-1	-3	+2	-1	-3	+2
n_i/mol	15	15(LR)	15	3(LR)	15	15
n_f/mol	10	0	25	0	6	21
$\Delta n/\text{mol}$	-5	-15	+10	-3	-9	+6
$\Delta\xi_{\text{max}}/\text{mol}$	5	5	5	3	3	3

Example 4

For any reaction, provided that we start with amounts of reactants equal to the stoichiometric coefficients in the equation, we will always have $\Delta\xi_{\text{max}} = 1$. This stage will be reached when (if) the reaction goes to completion.

	$\frac{1}{2}\text{N}_2 + \frac{1}{2}\text{H}_2 = \text{NH}_3$			$\text{N}_2 + 3\text{H}_2 = 2\text{NH}_3$			$2\text{N}_2 + 6\text{H}_2 = 4\text{NH}_3$		
ν	$-\frac{1}{2}$	$-\frac{1}{2}$	+1	-1	-3	+2	-2	-6	+4
n_i/mol	$\frac{1}{2}$	$\frac{1}{2}$	0	1	3	0	2	5	0
n_f/mol	0	0	1	0	0	2	0	0	4
$\Delta n/\text{mol}$	$-\frac{1}{2}$	$-\frac{1}{2}$	+1	-1	-3	+2	-2	-6	+4
$\Delta\xi/\text{mol}$	1	1	1	1	1	1	1	1	1

Some of the advantages of having $\Delta\xi$ vary over a fixed range of 0 to 1 were mentioned above. Example 4 shows how this may be achieved, without violating IUPAC specifications—by writing down a chemical equation and then specifying that the reaction starts with amounts of reactants equal to the stoichiometric coefficients in the equation.

Comments

If one is prepared to go beyond the limitations of IUPAC restrictions, then a simpler and more elegant solution is the reaction advancement ratio, χ , suggested by Dumon et al. (1), where $\chi = \Delta\xi/\Delta\xi_{\text{max}}$ and $\Delta\xi$ and $\Delta\xi_{\text{max}}$ have the definitions already given above. It would make even more sense if IUPAC were prepared to support the definition $\xi = \Delta\xi/\Delta\xi_{\text{max}}$. In this case there would be no need to introduce the new name and symbol suggested by Dumon and the new definition could become an extension of existing IUPAC recommendations. This definition would allow ξ to vary from 0 to 1 in the same way that $\Delta\xi$ varies in example 4 above. However, it would have the additional benefit of being an intensive, dimensionless quantity similar to a mole fraction and would thus be independent of the initial amounts of reactants.

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Effects of Hydrolysis on Determining the Solubility Product of Potassium Bitartrate

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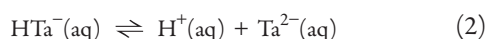
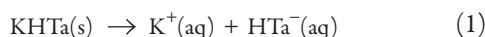
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Potassium bitartrate, $\text{KHC}_4\text{H}_4\text{O}_6$, symbolized below as KHTa, is a slightly soluble amphoteric salt of tartaric acid and is commonly known as “cream of tartar”. It is a byproduct of the wine making industry and is well known for its various uses in cooking and baking, especially as an acidic component of baking powder.

The determination of solubility and solubility products is a common undergraduate experiment. Because KHTa is inexpensive, safe, readily available, and well known to many students, it has become a popular subject of these experiments (1–8). The general procedure given in these references uses a standard hydroxide ion solution to titrate a saturated solution of KHTa. The solubility is then calculated directly from the amount of hydroxide ion, and the solubility product is calculated as the square of this solubility. Unfortunately, both calculations are faulty in principle because they ignore the fact that in aqueous solution the amphoteric HTa^- anion hydrolyzes to form H_2Ta and ionizes to form Ta^{2-} .

The analysis of the data described in refs 1–8 makes two incorrect assumptions. The first erroneous assumption is that the titration gives $[\text{HTa}^-]$; that is, it is assumed that $n(\text{OH}^-) = n(\text{HTa}^-)$. The second erroneous assumption is that $[\text{K}^+] = [\text{HTa}^-]$. It will be shown below that both assumptions are wrong and that the errors introduced by these assumptions produce an error in the solubility product that is not negligible. Throughout this article $[\text{X}]$ will represent the equilibrium concentration of X.

The equilibria in a saturated aqueous solution of KHTa are



The slight excess of $\text{H}^+(\text{aq})$ produced by eq 2 relative to the $\text{OH}^-(\text{aq})$ produced by eq 3 results in the saturated solution having a pH of 3.70 at 25 °C. Because of these reactions, the solubility of KHTa is given by either $[\text{K}^+(\text{aq})]$ or $\{[\text{H}_2\text{Ta(aq)}] + [\text{HTa}^-(\text{aq})] + [\text{Ta}^{2-}(\text{aq})]\}$ while the solubility product is given by $[\text{K}^+(\text{aq})][\text{HTa}^-(\text{aq})]$. It is therefore necessary to obtain both $[\text{K}^+(\text{aq})]$ and $[\text{HTa}^-(\text{aq})]$ to calculate the solubility product.

When the solution is titrated, all three acid species, $\text{H}^+(\text{aq})$, $\text{H}_2\text{Ta(aq)}$, and $\text{HTa}^-(\text{aq})$, react with the added $\text{OH}^-(\text{aq})$ ion, therefore

$$\begin{aligned} n\{\text{OH}^-(\text{aq})\} &= n\{\text{H}^+(\text{aq})\} + 2n\{\text{H}_2\text{Ta(aq)}\} + n\{\text{HTa}^-(\text{aq})\} \\ &= \{[\text{H}^+(\text{aq})] + 2[\text{H}_2\text{Ta(aq)}] + [\text{HTa}^-(\text{aq})]\}V \quad (4) \end{aligned}$$

Application of mass and charge balance (9) gives

$$[\text{K}^+(\text{aq})] = [\text{H}_2\text{Ta(aq)}] + [\text{HTa}^-(\text{aq})] + [\text{Ta}^{2-}(\text{aq})] \quad (5)$$

$$\begin{aligned} [\text{H}^+(\text{aq})] + [\text{K}^+(\text{aq})] &= [\text{HTa}^-(\text{aq})] + 2[\text{Ta}^{2-}(\text{aq})] + [\text{OH}^-(\text{aq})] \quad (6) \end{aligned}$$

Substituting eq 5 into eq 6 gives

$$[\text{H}^+(\text{aq})] + [\text{H}_2\text{Ta(aq)}] = [\text{Ta}^{2-}(\text{aq})] + [\text{OH}^-(\text{aq})] \quad (7)$$

If it is assumed that $[\text{OH}^-(\text{aq})]$ in the saturated solution is negligible, then $[\text{H}^+(\text{aq})] = [\text{Ta}^{2-}(\text{aq})] - [\text{H}_2\text{Ta(aq)}]$. Substituting this expression into eq 4 gives

$$\begin{aligned} n\{\text{OH}^-(\text{aq})\} &= \{[\text{H}_2\text{Ta(aq)}] + [\text{HTa}^-(\text{aq})] + [\text{Ta}^{2-}(\text{aq})]\}V \quad (8) \end{aligned}$$

which by eq 5 becomes equal to $[\text{K}^+(\text{aq})]V$, that is

$$[\text{K}^+(\text{aq})] = \frac{n\{\text{OH}^-(\text{aq})\}}{V} \quad (9)$$

Therefore the solubility can be calculated from the titration data provided $[\text{OH}^-(\text{aq})]$ in the saturated KHTa solution is neglected.

From eqs 9 and 4

$$\begin{aligned} [\text{K}^+(\text{aq})] &= [\text{H}^+(\text{aq})] \\ &+ \frac{2[\text{H}^+(\text{aq})][\text{HTa}^-(\text{aq})]}{K_{a1}(\text{H}_2\text{Ta})} + [\text{HTa}^-(\text{aq})] \quad (10) \end{aligned}$$

where $K_{a1}(\text{H}_2\text{Ta})$ is the first acid dissociation constant of tartaric acid. Rearrangement of eq 10 results in

$$[\text{HTa}^-(\text{aq})] = \frac{[\text{K}^+(\text{aq})] - [\text{H}^+(\text{aq})]}{1 + \frac{2[\text{H}^+(\text{aq})]}{K_{a1}(\text{H}_2\text{Ta})}} \quad (11)$$

Measurement of the pH before titration gives $[\text{H}^+(\text{aq})]$, therefore, $[\text{HTa}^-(\text{aq})]$ can be determined from the well-established value of $K_{a1}(\text{H}_2\text{Ta})$, and hence $K_{sp}(\text{KHTa})$ can be calculated.

Conclusion

By the simple expedient of measuring the initial pH of the solution and at the cost of a slightly more complicated calculation, this popular but flawed experiment can be transformed into an excellent freshman exercise. It may be noted that the above considerations apply not only to salts of amphoteric electrolytes; the existence of complications owing to hydrolysis may need to be considered for the salt of any weak electrolyte, depending on the values of the acid dissociation constants. The case of KHTa is somewhat unusual because the values of K_{a1} and K_{a2} are sufficiently similar for the saturated solution to contain significant amounts of all three tartrate-containing species.

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An Introductory Idea for Teaching Two-Component Phase Diagrams

Gavin D. Peckham^{*,†} and Ian J. McNaught[‡]

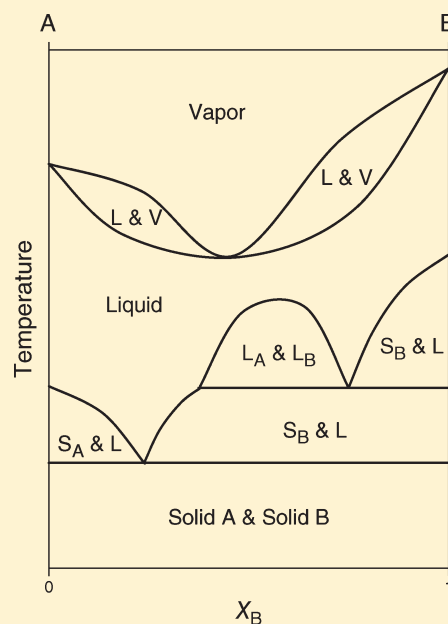
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S Supporting Information

ABSTRACT: Before teaching two-phase equilibria in the traditional piecemeal manner, it is proposed that an initial overview of a particular “complete” two-component phase diagram would be beneficial.

KEYWORDS: Upper-Division Undergraduate, Physical Chemistry, Misconceptions/Discrepant Events, Problem Solving/Decision Making, Equilibrium, Phases/Phase Transitions/Diagrams, Thermodynamics



The teaching of two-component phase diagrams has attracted little attention in this *Journal*,^{1–3} and it is hoped that this article will make a useful contribution. Current physical chemistry textbooks describe two-component phase diagrams adequately, but do so in a piecemeal fashion one section at a time; first solid–liquid equilibria, then liquid–vapor equilibria, and so on. We have found it pedagogically advantageous to introduce the teaching of two-component phase diagrams with a simple, stylized phase diagram that shows all of the various equilibria in a single sketch. A brief, general description of this initial diagram helps to “set the scene” before continuing with the traditional approach of describing the various possible combinations of equilibria, in detail, one at a time.

This suggested approach may be illustrated by an analogy—the assembly of a jigsaw puzzle. One could start by simply trying to fit individual jigsaw pieces together and then hoping to see the overall picture emerge as one goes along. In practice, however, it is much more helpful to first study the complete picture on the box. This gives a good overall idea of what to expect, where each individual piece is likely to go and how the individual areas are arranged with respect to one another.

Of all the partial two-component phase diagrams presented in textbooks, we have found that liquid–liquid phase diagrams are the least easily understood by our students in terms of how they

“fit” into a more extensive phase diagram for the system. For example, the water–phenol system is a classic case of a liquid–liquid system that appears in numerous physical chemistry textbooks; however, the complete phase diagram for this system does not appear in any current textbook, despite the fact that the necessary data are available in the literature.^{4–6} Although some textbooks do show phase diagrams that combine liquid–vapor equilibria at higher temperatures with liquid–liquid equilibria at lower temperatures, even these do not show how the liquid–liquid phase boundary “joins” onto the solid–liquid phase boundary at lower temperatures.

For the reasons detailed above, we have found Figure 1 to be useful. A stylized diagram with a minimum of labeling, such as Figure 1, is all that is required to introduce students to the general features of two-component diagrams. A set of similar diagrams, one simpler and one more complex than Figure 1, is provided in the Supporting Information.

At this initial stage, it is not necessary or even desirable to mention details such as eutectic points, azeotropes, and so forth. The purpose of starting with Figure 1 is to simply give a general overview of two-component systems and to show how different

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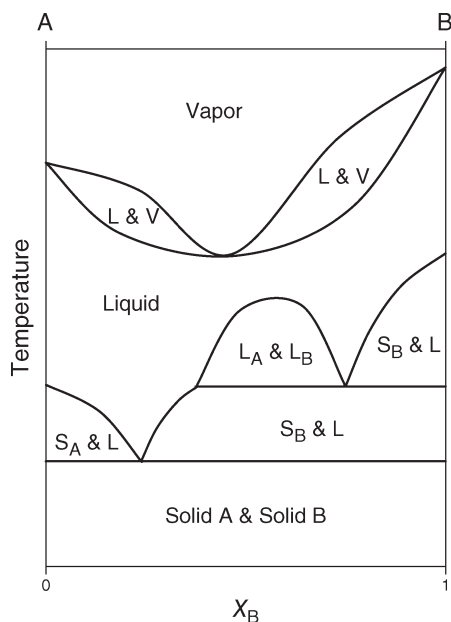


Figure 1. A stylized two-component phase diagram with strong positive deviations from Raoult's law and showing a region of liquid–liquid equilibrium (miscibility gap): S_A (solid A), S_B (solid B), L_A (liquid A), L_B (liquid B), L (liquid), and V (vapor).

phases exist, singly or in equilibrium, under different conditions of temperature and composition. Care should be taken to emphasize that the number of possible variations of these diagrams for various “real” systems is enormous. However, the same principles and methods of interpretation apply to them all. Having first presented the “big picture”, it is our experience that students find the subsequent, detailed discussions of its various sections more meaningful and thus emerge with a far better grasp of two-component phase diagrams.

■ ASSOCIATED CONTENT

Supporting Information

Diagrams showing a simpler and a more complex two-component system. This material is available via the Internet at <http://pubs.acs.org>.

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The Variation of Electrochemical Cell Potentials with Temperature

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S Supporting Information

ABSTRACT: Electrochemical cell potentials have no simple relationship with temperature but depend on the interplay between the sign and magnitude of the isothermal temperature coefficient, dE°/dT , and on the magnitude of the reaction quotient, Q . The variations in possible responses of standard and non-standard cell potentials to changes in the temperature, topics that are not discussed in any current textbook, are described.

KEYWORDS: Second-Year Undergraduate, Physical Chemistry, Misconceptions/Discrepant Events, Problem Solving/Decision Making, Electrochemistry, Electrolytic/Galvanic Cells/Potentials

Electrochemical cell potential variation with temperature is clear from the Nernst equation, which is routinely included in introductory and physical chemistry textbooks,¹

$$E = E^\circ - (RT/nF) \ln Q \quad (1)$$

where E° is the standard electrode potential, R is the gas constant, T is the absolute temperature, n is the amount of electrons, F is the Faraday constant, and Q is the reaction quotient. However, the explicit nature of this variation of cell potential with temperature is not discussed at the introductory level nor in more advanced textbooks of physical chemistry that are in current use.

The response of E° to temperature changes is entirely determined by the sign of the temperature coefficient of the electrode, dE°/dT . Within the accuracy of most electrochemical measurements, the variation of E° with temperature² can be described by

$$E^\circ(T_2) = E^\circ(T_1) + (dE^\circ/dT)(T_2 - T_1) \quad (2)$$

However, the response of the actual electrode potential, E , is determined by the interplay between the sign and magnitude of dE°/dT ^{2,3} and the magnitude of Q . This interplay may have various possible outcomes as indicated below.

Consider an electrode with a negative temperature coefficient, so that the standard electrode potential, E° , will decrease as the temperature is raised. Depending on the magnitude of Q in the Nernst equation, the electrode potential, E , may either rise or fall as the temperature is increased. More specifically, provided Q is independent of temperature, it can be shown that the temperature dependence of E depends only on the sign of

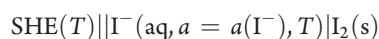
$$(dE^\circ/dT) - (R/nF) \ln Q$$

If this expression is positive, E will increase with a rise in temperature, and if the expression is negative, E will decrease with a rise in

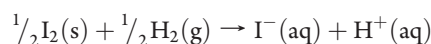
temperature. For a given electrode, the “changeover” point between these two responses will occur when

$$(dE^\circ/dT) = (R/nF) \ln Q \quad (3)$$

As an example, consider the following cell



for which the overall cell reaction may be written as



where $n = 1$ and $Q = a(\text{I}^-)a(\text{H}^+) = a(\text{I}^-)$, where a is the activity. By definition, both $E^\circ(\text{SHE})$ and $dE^\circ(\text{SHE})/dT$ are zero at all temperatures, therefore

$$E_{\text{cell}} = E[\text{I}^-(\text{aq}, a = a(\text{I}^-), T) | \text{I}_2(\text{s})] = E^\circ[\text{I}^-(\text{aq}, T) | \text{I}_2(\text{s})] - (RT/F) \ln Q$$

For the $\text{I}^-(\text{aq}) | \text{I}_2(\text{s})$ half cell at 25 °C, it has been established² that $E^\circ[\text{I}^-(\text{aq}, T) | \text{I}_2(\text{s})] = 0.5355 \text{ V}$ and $dE^\circ[\text{I}^-(\text{aq}, T) | \text{I}_2(\text{s})]/dT = -0.148 \text{ mV/K}$. Substituting this value of dE°/dT into eq 3 gives $Q = 0.180 = a(\text{I}^-)$. This is the activity at which the cell potential is independent of temperature.

For a cell with $a(\text{I}^-) > 0.180$, the value of $[(dE^\circ/dT) - (R/F) \ln Q]$ will be negative and E_{cell} will decrease as temperature rises. Conversely, for a cell with $a(\text{I}^-) < 0.180$, the value of $[(dE^\circ/dT) - (R/F) \ln Q]$ will be positive and E_{cell} will increase as temperature rises, despite the fact that this same temperature rise is simultaneously causing E°_{cell} to decrease. Some numerical results to illustrate these points are given in Table 1.

It should be clear from this example and from the foregoing discussion that the variation of a cell potential has no simple and direct relationship with temperature but depends instead on the interaction between the sign and magnitude of the

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Table 1. The Variation of E° and E with Concentration and Temperature for the Cell, $\text{SHE}(T)||\text{I}^-(\text{aq}, a = a(\text{I}^-), T)|\text{I}_2(\text{s})$

Temperature/ $^\circ\text{C}$	$E^\circ_{\text{cell}}/\text{V}$	E_{cell}/V $a(\text{I}^-) = 0.100$	E_{cell}/V $a(\text{I}^-) = 0.180$	E_{cell}/V $a(\text{I}^-) = 0.300$
5	0.5385	0.5937	0.5796	0.5674
25	0.5355	0.5947	0.5796	0.5664
45	0.5325	0.5956	0.5796	0.5655

temperature coefficient, $\text{d}E^\circ/\text{d}T$, and the magnitude of the reaction quotient, Q .

■ ASSOCIATED CONTENT

■ Supporting Information

An abridged table of $\text{d}E^\circ/\text{d}T$ data. This material is available via the Internet at <http://pubs.acs.org>.

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The Octant Rule: Check UPFRont!

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S Supporting Information

ABSTRACT: The importance of considering substituents in the front half of the space is demonstrated when applying the octant rule.

KEYWORDS: Upper-Division Undergraduate, Organic Chemistry, Computer-Based Learning, Diastereomers, Enantiomers, Stereochemistry

The empirical octant rule¹ has played an important role in determining the stereochemistry of naturally occurring chiral ketones. Its application to several molecules has been described previously in this *Journal*.² A recent article³ has shown an attractive way to display molecules and decide if they would show a positive or a negative Cotton effect. However, the technique described will only work if the contributing groups lie in the rear of the molecule, that is, behind the carbonyl group. The first step in applying the octant rule should be to divide the groups into those that are in the front half of space (in front of the carbonyl group) and those that are in the rear half (behind the carbonyl group). This communication describes the steps necessary to apply the octant rule when there are groups in front and/or behind the carbonyl group.

In applying the octant rule, space around the carbonyl chromophore is divided into octants via three planes based upon nodes in the electronic wave function, and then the regions are given signs equivalent to the product xyz (in a left-handed coordinate system), giving rise to the mnemonic UPFRont, Upper Positive Front Right.⁴ Two of those planes (xz and yz) are determined from the local symmetry of the carbonyl group and its attachments. The third plane (S) required to divide space into eight regions was originally placed perpendicular to the xz and yz planes at the center of the $C=O$ bond. This is demonstrated with cyclohexanone (Figure 1A) with the $C=O$ bond horizontal along the z axis.⁵ However, a later study showed that the third plane, S , should be placed further behind the carbonyl bond along the z axis (Figure 1B) and curved toward the carbonyl group, cutting the cyclohexane ring just behind C3 and C5.⁶

EXAMPLE

The technique will be illustrated using the molecules that first unambiguously demonstrated the need for an octant rather than a quadrant rule,⁷ *syn*-(1*R*)-spiro[cyclobutan-2-one-1,2'-(4'(a)-methyladamantane)] and its anti isomer⁸ (Figure 2, panels A and B, respectively).

To make this approach more generally available, the commercial drawing program used by Kang and Kang³ has been replaced by the freeware, ChemSketch.⁹ The methyl group is the only group introducing dissymmetry into the

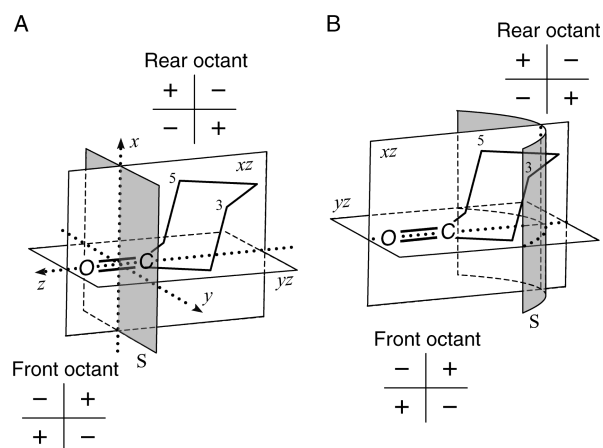


Figure 1. Orientation of the carbonyl chromophore in cyclohexanone and signs of the octants when (A) the S plane is perpendicular to the center of the carbonyl group and (B) the S surface lies behind the carbonyl group and is curved.

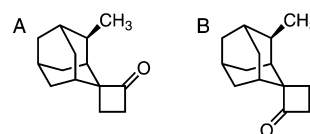


Figure 2. Structures of (A) *syn*-(1*R*)-spiro[cyclobutan-2-one-1,2'-(4'(a)-methyladamantane)] and (B) the anti isomer.

molecule; all of the other atoms have symmetrically disposed counterparts that compensate for any rotation of the electric field vector. Figure 3 shows that, for the *syn* isomer, the methyl group (green) lies in front of the carbonyl group (red), whereas for the *anti* isomer, it lies behind the carbonyl group. Rotating the molecules so that the carbonyl group points directly toward the observer, it is clear from Figure 4 that the *syn* isomer has the methyl group (green) in the Upper Front Left (−) octant, whereas the *anti* isomer has the methyl group in the Upper Rear Right (−) octant. The experimental circular dichroism spectra⁷ agree with these predictions.

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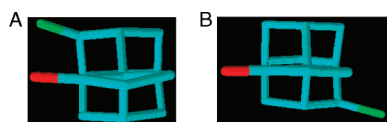


Figure 3. ChemSketch drawings of (A) the syn isomer with the methyl group (green) in front of the carbonyl group (red) and (B) the anti isomer with the methyl group behind the carbonyl group.

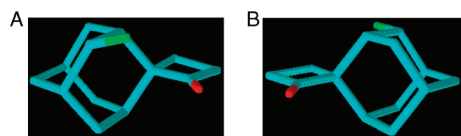


Figure 4. ChemSketch drawings of (A) the syn isomer with the methyl group Upper, Front, Left (–) and (B) the anti isomer with the methyl group Upper, Rear, Right (–).

A step-by-step illustration using ChemSketch to compare (1*R*)-*exo*-2-methylcyclo[2.2.1]heptan-7-one and (1*R*)-*endo*-2-methylcyclo[2.2.1]heptan-7-one is given in the Supporting Information.

■ ASSOCIATED CONTENT

§ Supporting Information

Details of how to use ChemSketch to produce diagrams such as those in Figures 3 and 4. This material is available via the Internet at <http://pubs.acs.org>.

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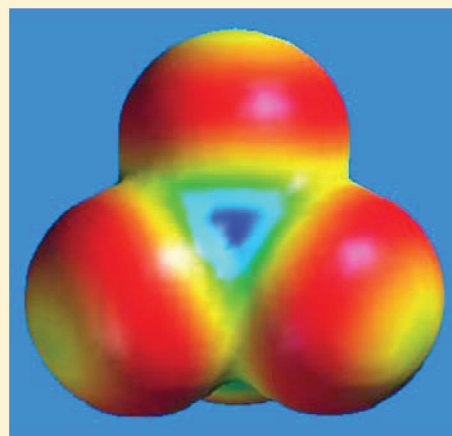
Teaching Intermolecular Forces to First-Year Undergraduate Students

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ABSTRACT: A recent article in this *Journal* provides an excellent overview of intermolecular forces of attraction (IMFs) at a first-year level by using plots of boiling point versus the number of electrons per molecule for the hydrides of groups IV–VII. However, references to IMFs in introductory chemistry courses are typically extended to other physical properties, such as melting point, viscosity, surface tension, and so forth. At the first-year level, we feel that a degree of circumspection is required lest it be assumed that all of these physical properties necessarily have a similar, simple correspondence to IMFs as that which is generally shown by boiling points.



KEYWORDS: First-Year Undergraduate/General, Physical Chemistry, Misconceptions/Discrepant Events, Noncovalent Interactions, Physical Properties

Glazier, Marano, and Eisen's¹ approach to teaching intermolecular forces of attraction (IMFs) using plots of boiling points versus the number of electrons per molecule for the hydrides of groups IV–VII is highly recommended. In addition to a systematic, evidence-based approach to understanding IMFs, they also draw attention to various pitfalls, particularly the widespread misconception that dispersion (London) forces are of negligible strength when compared with hydrogen-bonding and dipole–dipole (Keesom) forces.

Glazier et al.¹ make the point that dispersion forces, and thus boiling points, are expected to increase as the number of electrons per molecule increases. However, the data in Table 1

Table 1. Boiling Points of Some Group IV Tetrahalides

Compound	Molar Mass/ (g mol ⁻¹)	Number of Electrons	Boiling Point/ °C
CCl ₄	153.82	74	+77
SiCl ₄	169.90	82	+58
CBr ₄	331.63	146	+190
SiBr ₄	347.70	154	+155

illustrate the anomalous behavior of the boiling points of some group IV tetrahalides (which only exhibit dispersion forces). The electronegativity difference between the atoms in the Si–X bond, and thus the polarity of this bond, is significantly greater than that in the C–X bond. Despite the slightly polar bonds in CX₄ and the significantly polar bonds in SiX₄, both molecules are nonpolar overall because of their symmetry. However, the

halide ends of the bonds, which are located at the outer regions of each molecule, are slightly negative because of the bond dipoles. The other end of the bond dipole (C or Si) is slightly positive and located at the middle of the molecule. Therefore, when viewed from a distance, the outer regions, or “surface”, of both the CX₄ and the SiX₄ molecules have a slight excess of negative charge. This excess of negative surface charge is significantly larger in the case of SiX₄ because of its greater bond dipoles. The electrostatic repulsion between these surface charges slightly reduces the attractive forces between adjacent molecules in the liquid phase. This effect is sufficiently great in the case of SiX₄ to reduce the boiling point below the value that would be expected on the basis of dispersion forces alone. For boiling points, very few examples that show this type of anomalous behavior are found. This supports the well-argued contention of Glazier et al.¹ that boiling points are a reasonably good measure of the strength of IMFs.

Glazier et al.¹ note that vaporization enthalpies are a more direct measure of the strength of IMFs than boiling points, but do not mention that vapor pressures are also a good measure of the strength of IMFs. They have explained why they prefer to concentrate on boiling points rather than vaporization enthalpies at the first-year level. We concur with them and will do the same, but ask the reader to bear in mind that both boiling points and vapor pressures are strongly correlated with

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vaporization enthalpies and that these three closely interrelated properties rarely show anomalous behavior.

Introductory courses and textbooks typically extend the role of IMFs to many other physical properties, such as melting point, viscosity, surface tension, and so forth.² We feel that first-year students need to be made acutely aware that correlating IMFs to these physical properties is not necessarily as straightforward as is the case with the generally “well-behaved” boiling points. In an introductory course, this may require no more than a few words stating explicitly that, although melting point, viscosity, surface tension, and so forth are affected by IMFs, these physical properties do **not** necessarily display the same neat correlation with IMFs as is generally shown by the boiling points.

SOME APPARENT ANOMALIES

For each of the physical properties mentioned above, it is always possible to judiciously select a few compounds and tabulate the relevant data to illustrate a correlation between that property and the corresponding IMFs. However, doing this may mistakenly lead students to believe that IMFs are the sole influence that needs to be considered. For example, the data for some silanes (Table 2) could be used to impress students with

Table 2. Melting Points and Boiling Points of Some Silanes

Compound	Molar Mass/ (g mol ⁻¹)	Number of Electrons	Melting Point/°C	Boiling Point/°C
Silane, SiH ₄	32.12	18	-185	-112
Disilane, Si ₂ H ₆	62.22	34	-129	-15
Trisilane, Si ₃ H ₈	92.32	60	-117	+53

the direct correlation of IMFs, not only with boiling points, but also with melting points (ref 3, Section 4). These molecules exhibit only dispersion forces, which increase in strength with the number of electrons per molecule. Thus, we would expect an increase in melting points and boiling points with the number of electrons per molecule. This trend is found in the table. Sadly, the illusion created by this convenient example is dispelled by similar data for some alcohols (Table 3) (ref 3,

Table 3. Melting Points and Boiling Points of Some Alcohols

Compound	Molar Mass/ (g mol ⁻¹)	Number of Electrons	Melting Point/°C	Boiling Point/°C
Methanol, CH ₃ OH	32.04	18	-98	+65
Ethanol, C ₂ H ₅ OH	46.07	26	-114	+78
Propan-1-ol, C ₃ H ₇ OH	60.10	34	-124	+97

Section 3). Here, the increase in the boiling points correlates neatly with the expected increase in IMFs. However, in defiance of expectations, the melting points show exactly the opposite trend.

A similar situation arises for viscosity. Consider the isomers of butanol. As shown in Table 4, these isomers have the same molar mass, number of electrons, and one hydrogen bond. However, their dispersion forces are affected by their shape. “Long, thin” molecules such as butan-1-ol can make greater surface contact with one another and thus have greater dispersion forces than is the case for more spherical or

Table 4. Boiling Points and Viscosities of Some Isomers of Butanol

Compound	Molar Mass/ (g mol ⁻¹)	Number of Electrons	Boiling Point/ °C	Viscosity/ (mPa s) (at 30 °C)
Butan-1-ol	74.12	46	+117.7	2.271
2-Methylpropan-1-ol	74.12	46	+107.9	2.842
2-Methylpropan-2-ol	74.12	46	+82.4	3.378

“globular” molecules of a similar size. Thus, the IMFs in these molecules are expected to decrease the more spherical the isomers become. Hence, a “long, thin” molecule such as butan-1-ol has stronger dispersion forces than its more “globular” isomer, 2-methylpropan-1-ol, and its even more “globular” isomer, 2-methylpropan-2-ol. As usual, the boiling points of these isomers support this contention; however, their viscosities⁴ show a strong and unexpected trend in the opposite direction.

The surface tensions (ref 5, Table 6) of a homologous series of esters are shown in Table 5. Yet again, the increase in the

Table 5. Boiling Points and Surface Tensions of Homologous Esters

Compound	Molar Mass/ (g mol ⁻¹)	Number of Electrons	Boiling Point/ °C	Surface Tension/ (mN m ⁻¹) (at 20 °C)
Methyl chloroacetate	108.52	56	+130	35.3
Ethyl chloroacetate	122.55	64	+143	31.8
Propyl chloroacetate	136.58	72	+161	30.7
Butyl chloroacetate	150.60	80	+183	30.2

boiling points correlates neatly with the expected increase in IMFs, whereas the surface tension, in defiance of expectations, shows exactly the opposite trend.

DISCUSSION

The following discussion briefly accounts for the expected correlation between IMFs and various physical parameters. Accounting for the many deviations from expected behavior requires diverse and complex explanations that are not given here.

The best readily available measure of IMFs in a liquid is the enthalpy of vaporization, $\Delta_{\text{vap}}H$. For any phase change, $T = \Delta H/\Delta S$; therefore, $T_{\text{bp}} = \Delta_{\text{vap}}H/\Delta_{\text{vap}}S$, where $\Delta_{\text{vap}}S$ is the entropy of vaporization. Also, for a majority of molecules that are not hydrogen bonded, $\Delta_{\text{vap}}S \approx 10.5R$, where R is the gas constant (Trouton's rule),⁶ so $T_{\text{bp}} \propto \Delta_{\text{vap}}H$, making the boiling points a good measure of IMFs, as indicated by Glazier et al.¹ Provided the temperature is not too close to the critical temperature, vapor pressures are directly correlated with $\Delta_{\text{vap}}H$ through the Clausius–Clapeyron equation,⁷ so the vapor pressures are also good measures of IMFs under those circumstances.

The best readily available measure of IMFs in a solid is the enthalpy of fusion, $\Delta_{\text{fus}}H$. At the melting point, $T_{\text{mp}} = \Delta_{\text{fus}}H/\Delta_{\text{fus}}S$. Anomalies in the melting point can arise either from the enthalpy term or the entropy term.⁸ It was observed a long time ago that symmetric molecules usually have an unexpectedly high melting point.⁹ One reason for this is that $S(\text{solid})$ for a

symmetric molecule contains an additional $R \ln \sigma$ term relative to an unsymmetric molecule, where σ is the symmetry number.¹⁰ This additional residual entropy does not exist in the liquid phase, so $\Delta_{\text{fus}}S$ for a symmetric molecule is less than $\Delta_{\text{fus}}S$ for an unsymmetric molecule, resulting in an unexpectedly high melting point; however, see work by Pinal¹¹ for a discussion of cases where the symmetric molecule shows the opposite behavior. For unsymmetric molecules, $\Delta_{\text{fus}}S \approx aR$, where a takes different values for different types of solids: $a \approx 6.8$ for ordered crystals of rigid molecules,¹² $a \approx 2-5$ for partially disordered crystals, and $a \approx 0.5-2$ for highly disordered crystals.¹³ This large variation in a for different types of solids means that the melting point is not as well correlated with $\Delta_{\text{fus}}H$, and so it is more likely to show anomalous behavior. Ionic compounds have high melting points because of the isotropic nature of the attractive forces between the ions. The greater the degree of covalency in the bonding, the more directional the forces in the crystal become. It follows from Fajans' rules¹⁴ that increased covalency is associated with more polarizing cations (high charge, small radius) and more polarizable anions (high charge, large radius). An increase in covalency leads to strong bonds in particular directions, but weakened forces in other directions. It is only necessary to disrupt the weaker forces to produce melting, resulting in lower melting points for ionic compounds showing high covalent character (compare AlBr_3 , strong directional forces in the layers, weak forces between the layers, melting point = 97 °C, with NaF , strong isotropic forces in all directions, melting point = 993 °C).

Viscosity depends both on IMFs and molecular structure. The less spherical the molecules, the greater the tendency to become entangled, making it more difficult for the molecules to move past each other, thereby increasing the viscosity. This dependence of viscosity on molecular structure, particularly the length of the molecule, reduces the correlation with IMFs.

The surface tension measures the change in Gibbs energy when the surface area is increased at constant pressure. It therefore depends on a difference in enthalpy and entropy contributions ($G = H - TS$) rather than the ratio relevant to boiling and melting points. Along a homologous series, an increase in the enthalpy term may dominate (surface tension increases) or an increase in the entropy term may dominate (surface tension decreases), as is the case in Table 5.

There is almost no limit to the data that can be produced, both in support of, and in disagreement with, a correlation between some physical property and the corresponding IMFs. This being the case, it is likely to be counterproductive to provide students with a series of judiciously selected examples for physical properties other than boiling points and vapor pressures.

CONCLUSION

We strongly recommend the approach of Glazier et al.¹ to the teaching of IMFs at the first-year level. However, we feel that first-year students must also be made acutely aware that, although IMFs make a significant contribution to almost all physical properties of matter, the correlation of IMFs with many physical properties is not necessarily as straightforward as is generally the case with boiling points and vapor pressures.

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Notes

The authors declare no competing financial interest.

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